90554-86-2; 2-hexadecanone, 18787-63-8; pentadecanal, 2765-11-9; *n*-octadecane, 593-45-3; *n*-pentadecyl acetate, 629-58-3; 1-hexadecanol, 36653-82-4; heptadecanal, 629-90-3; methyl *n*-pentadecanoate, 7132-64-1; 2-heptadecanone, 2922-51-2; 1-nonadecene, 18435-45-5; *O*-methyloxime hexadecanal, 68942-06-3; *n*-dodecanamide, 1120-16-7; *n*-nonadecane, 629-92-5; *N*-nonylacetamide, 45108-98-3; *N*-ethyloctanamide, 54007-35-1; *n*-tridecylcyclohexane, 6006-33-3; octadecanal, 638-66-4; *n*-eicosene, 27400-78-8; *n*-eicosane, 112-95-8; *n*-tetradecylcyclohexane, 1795-18-2; 1-octadecanol, 112-92-5; *n*-heptadecyl acetate, 822-20-8.

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L-Ornithyltaurine, a New Salty Peptide

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In a series of studies of the structure–bitter taste relationship of BPIa (H-Arg-Gly-Pro-Pro-Phe-Ile-Val-OH) from casein hydrolysate, the synthesized N-terminus analogues of BPIa, H-L-Orn-Gly-OH·HCl and H-L-Lys-Gly-OH·HCl, were fortuitously discovered to possess an "umami" taste about half as strong as that of monosodium glutamate (MSG), as well as a slightly salty taste. To characterize salty peptides, various analogues in which constituent amino acids were substituted were synthesized and their tastes measured. Among them, H-L-Orn-β-Ala-OH·HCl and H-L-Orn-Tau·HCl (L-ornithyl-2-aminoethanesulfonic acid hydrochloride) exhibited a salty taste equal to or greater than that of sodium chloride (NaCl), and most of the above peptides possessed an umami taste approaching or equal to that of MSG. These salty and umami peptides do not contain sodium ion in the molecules. We expect that these peptides will be useful as a new type of artificial seasoning instead of NaCl and MSG, in which the sodium content could be undesirable for diabetics and hypertensives.

In recent years, many investigators examined the chemical properties of various bitter, sweet, and sour peptides. Those peptides number about 1000. Of these, bitter peptides represent about 80%. Some have been isolated from natural foodstuffs such as cheese (Hamilton et al., 1974), natto (Maekawa and Tamai, 1965), sake (Takahashi et al., 1974), and cocoa (Pickenhangen and Dietrich, 1975). It is well-known that hydrolysis of protein with proteolytic enzymes is usually accompanied by formation of a bitter taste due to the production of bitter peptides (Yamashita et al., 1969; Arai et al., 1970; Matoba et al., 1970; Minamiura et al., 1972a,b). In addition, many workers have synthesized various bitter peptides and reported the relationship between bitter taste and chemical structure (Shiba and Nunami, 1974; Matoba and Hata, 1972; Okai, 1977; Fukui et al., 1983; Otagiri et al., 1983; Miyake et al., 1983). As for sweet peptides, aspartame (H-Asp-Phe-OMe) and its derivatives have been studied for the development of artificial sweetening agents (Mazur et al., 1969, 1970, 1973; Fujino et al., 1973, 1976; Ariyoshi et al., 1974; Ariyoshi, 1976, 1980; Miyoshi et al., 1978). Aspartame is now being marketed for dietary purposes.

Acidic peptides containing aspartyl and/or glutamyl residues usually possess a sour taste. Sweet and sour peptides account for about 15% of sapid peptides.

Other sapid peptides are rare. Fujimaki et al. (1973) reported some di- or tripeptides possessing an "umami" (MSG-like) taste that were obtained from an enzymatic digest of fish protein. Arai et al. (1973) prepared 12 kinds of dipeptides containing a glutamyl residue and discussed the relationship between umami taste and physicochemical properties. Yamasaki and Maeda (1978) also isolated a delicious peptide from extract of beef treated with papain

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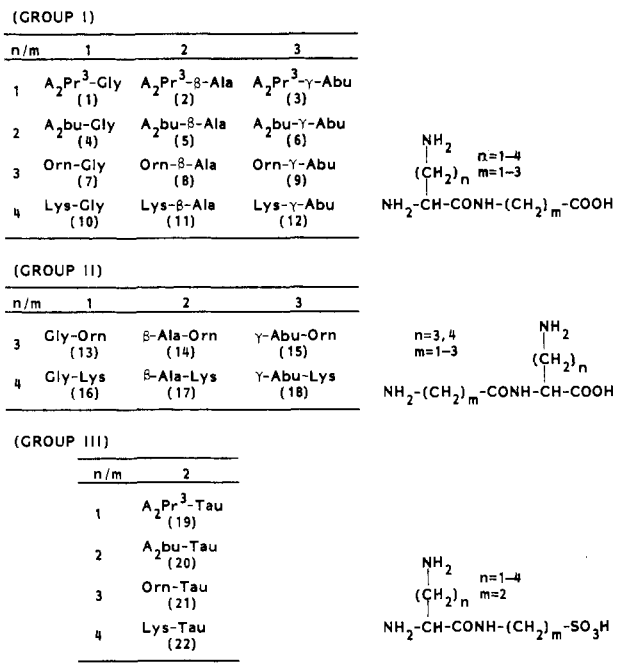

Figure 1. Synthesized dipeptides.

and determined its primary structure to be H-Lys-Gly-Asp-Glu-Glu-Ser-Leu-Ala-OH. Thus, several kinds of sapid peptides have been found. However, peptides possessing a salty taste, which is one of the four primary taste qualities, had not as yet been reported.

We studied the structure–taste relationship of the bitter peptide BPIa (H-Arg-Gly-Pro-Pro-Phe-Ile-Val-OH) isolated from casein hydrolysate by bacterial proteinase (Minamiura et al., 1972a,b), and we systematically synthesized its many analogues. To ascertain the role of the N-terminal arginyl residue for bitterness in BPIa, we attempted to substitute for it other basic amino acids such as ornithine and lysine. In the course of preparing those analogues, H-L-Orn-Gly-OH·HCl (**7**) and H-L-Lys-Gly-OH·HCl (**10**) (see Table IV) were discovered to exhibit an umami and a salty taste, with the umami taste being slightly stronger.

To elucidate the structure–salty taste relationship and further to develop new salty peptides, three groups of dipeptides as shown in Figure 1, whose structures were based on H-L-Orn- (or Lys)-Gly-OH, were synthesized and their tastes measured. First, 12 analogues (compounds **1–12**) in which the side chain length of the basic amino acid was changed and/or the methylene group of the glycyl residue was elongated, were examined in order to investigate the influence of skeletal and side chain lengths (group I). Next, we synthesized the peptides possessing the reverse of the amino acid sequences of group I, to learn the situational relationship of the basic amino acid for exhibiting the taste (compounds **13–18**, group II). Finally, four peptides (compounds **19–22**) in which the carboxyl group of group I was substituted by a sulfonyl group were prepared (group III).

EXPERIMENTAL SECTION

General. All the melting points are uncorrected. The thin-layer chromatography was carried out on Merck silica gel G with the two solvent systems: R_{f1}, 1-butanol–acetic acid–pyridine–water (4:1:1:2 v/v); R_{f2}, chloroform–methanol (5:1 v/v). Spots of materials possessing a free amino group on a thin-layer plate were detected by spraying ninhydrin and those of amino group blocked materials by spraying 25% hydrogen bromide in acetic acid and then ninhydrin. The optical rotations were measured on a Union PM-101 polarimeter. Prior to analyses, the compounds were dried over phosphorus pentoxide at 66 °C and 2 mmHg (1 mmHg = 133 Pa) for 4 h.

Sensory Analysis. The tastes of the peptides were organoleptically determined by panel evaluation employing four people. A descending concentration series, with each sample half the strength of its predecessor, were prepared. Before the sample was tasted, the mouth was throughly rinsed with deionized water. The sample solution was held in the mouth for ca. 10 s and then expectorated, and the threshold value and the taste quality were determined.

The threshold values were averaged after several examinations by the panelists with given peptides. The salty quality of peptides was compared with a standard NaCl solution. It was evaluated on a score of 0, 1, 2, 3, 4, and 5, wherein 5 was judged to be equivalent in salty taste to a reference 6.40 mM NaCl solution, whose concentration corresponds to twice its threshold value. Scores of 4, 3, 2, and 1 indicated descending degree of saltyness, compared with the reference solution. Score 0 indicates tastelessness or other tastes.

For umami taste, the same methods were employed with 3.12 mM MSG solution as a reference.

The results of sensory tests are listed in Table IV.

Syntheses of Group I. The peptides of group I were synthesized by conventional methods. Dibenzyloxycarbonyl amino acid and amino acid benzyl ester were condensed to yield the corresponding dibenzyloxycarbonyl dipeptide benzyl ester by the mixed anhydride method. The protecting groups of the dipeptide derivatives were removed by catalytic hydrogenation in acetic acid solution. The products were treated with HCl–dioxane and obtained as hydrochloride forms. The purities of the synthetic peptides and their intermediates were confirmed by melting points, optical rotation, thin-layer chromatography in two solvent systems, and elemental analyses.

L-(1,2-Diaminopropionyl)glycine Hydrochloride (**1**). Cbz-L-A_2Pr^3 (β-Cbz)-OH·DCHA (dicyclohexylamine salt) (2.77 g, 5 mmol) was dissolved in ethyl acetate (30 mL), and 1 M sulfuric acid (10 mL) was added to the mixture with stirring. The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated to dryness in vacuo, and the oily residue was dissolved in tetrahydrofuran (10 mL) and *N*-methylmorpholine (0.55 mL, 5 mmol). Ethyl chloroformate (0.50 mL, 5 mmol) was added to the mixture at −5 °C. After 15 min, a solution of H-Gly-OBzl·TsOH (1.96 g, 5 mmol) and *N*-methylmorpholine (0.55 mL, 5 mmol) in *N*,*N*-dimethylformamide (10 mL) was added to the mixture. The reaction mixture was stored in an ice bath for 1 h and then at room temperature overnight. The mixture was evaporated in vacuo and diluted with ethyl acetate. The solution was washed successively with water, 2% hydrochloric acid, water, 4% sodium bicarbonate, and water, and then dried over anhydrous sodium sulfate. The filtrate was evaporated in vacuo. The oily residue was crystallized from ether and petroleum ether to give Cbz-L-A_2Pr^3 (β-Cbz)-Gly-OBzl.

A solution of Cbz-L-A_2Pr^3 (β-Cbz)-Gly-OBzl (0.62 g, 1.2 mmol) in acetic acid (5 mL) was hydrogenated in the presence of palladium black at room temperature for 3 h. The catalyst was removed by filtration, and the filtrate was evaporated in vacuo. The residue was solidified by the aid of 5.6 M HCl–dioxane (0.21 mL, 1.2 mmol) and ethanol. The product was obtained as a hygroscopic substance.

Compounds **2–12** were obtained by the same method as described above. The physical properties of the synthetic peptides are given in Table I.

Table I. Yields and Analytical Data of Synthetic Peptides in Group I

compd	yield, %	mp, °C	$[\alpha]_D^{23}$, deg (solvent)	formula	found (calcd), % C	H	N	R_{f1}	R_{f2}
Cbz-A_2Pr^3(β-Cbz)-Gly-OBzl	68	101	−14 (c 1, DMF)	$C_{28}H_{29}O_7N_3$	64.70 (64.73)	5.62 (5.63)	7.85 (8.09)	0.94	0.78
Cbz-A_2Pr^3(β-Cbz)-β-Ala-OBzl	69	101–103	−9 (c 1, DMF)	$C_{29}H_{31}O_7N_3$	65.33 (65.28)	5.90 (5.86)	7.60 (7.88)	0.99	0.82
Cbz-A_2Pr^3(β-Cbz)-γ-Abu-OBzl	90	130–131	−9 (c 1, DMF)	$C_{30}H_{33}O_7N_3$	65.77 (65.80)	6.09 (6.07)	7.71 (7.67)	0.99	0.84
Cbz-A_2bu(γ-Cbz)-Gly-OBzl	70	111	−14 (c 1, DMF)	$C_{29}H_{31}O_7N_3$	65.24 (65.28)	5.86 (5.86)	7.84 (7.88)	0.99	0.80
Cbz-A_2bu(γ-Cbz)-β-Ala-OBzl	99	88–89	−6 (c 1, DMF)	$C_{30}H_{33}O_7N_3$	65.55 (65.80)	6.01 (6.07)	7.37 (7.67)	0.99	0.83
Cbz-A_2bu(γ-Cbz)-γ-Abu-OBzl	73	138	−2 (c 1, DMF)	$C_{31}H_{35}O_7N_3$	66.48 (66.29)	6.52 (6.28)	7.27 (7.48)	0.99	0.84
Cbz-Orn(δ-Cbz)-Gly-OBzl	90	151	−6 (c 1, DMF)	$C_{30}H_{33}O_7N_3$	65.69 (65.80)	6.03 (6.07)	7.76 (7.67)	0.99	0.84
Cbz-Orn(δ-Cbz)-β-Ala-OBzl	97	157	−2 (c 1, DMF)	$C_{31}H_{35}O_7N_3$	66.21 (66.29)	6.28 (6.28)	7.26 (7.48)	0.99	0.90
Cbz-Orn(δ-Cbz)-γ-Abu-OBzl	72	139	+2 (c 1, DMF)	$C_{32}H_{37}O_7N_3$	66.46 (66.76)	6.56 (6.48)	7.06 (7.30)	0.99	0.93
Cbz-Lys(ε-Cbz)-Gly-OBzl	81	129	−11 (c 1, DMF)	$C_{31}H_{35}O_7N_3$	66.30 (66.29)	6.31 (6.28)	7.50 (7.48)	0.99	0.82
Cbz-Lys(ε-Cbz)-β-Ala-OBzl	81	85	−4 (c 1, DMF)	$C_{32}H_{37}O_7N_3$	66.72 (66.76)	6.51 (6.48)	7.40 (7.30)	0.99	0.91
Cbz-Lys(ε-Cbz)-γ-Abu-OBzl	96	139	−3 (c 1, DMF)	$C_{33}H_{39}O_7N_3$	66.96 (67.21)	6.80 (6.67)	6.87 (7.13)	0.99	0.94
H-A_2Pr^3-Gly-OH·HCl (1)	100	hygroscopic						0.10	0
H-A_2Pr^3-β-Ala-OH·HCl (2)	79	hygroscopic	+21 (c 1, H_2O)					0.28	0
H-A_2Pr^3-γ-Abu-OH·HCl (3)	97	hygroscopic	+21 (c 1, H_2O)					0.32	0
H-A_2bu-Gly-OH·HCl (4)	100	hygroscopic						0.25	0
H-A_2bu-β-Ala-OH·HCl (5)	87	hygroscopic	+12 (c 1, H_2O)					0.25	0
H-A_2bu-γ-Abu-OH·HCl (6)	81	hygroscopic	+21 (c 1, H_2O)					0.23	0
H-Orn-Gly-OH·HCl (7)	100	hygroscopic	+23 (c 1, AcOH)					0.13	0
H-Orn-β-Ala-OH·HCl (8)	100	hygroscopic	+28 (c 1, AcOH)					0.16	0
H-Orn-γ-Abu-OH·HCl (9)	100	hygroscopic						0.21	0
H-Lys-Gly-OH·HCl (10)	100	hygroscopic						0.35	0
H-Lys-β-Ala-OH·HCl (11)	64	hygroscopic	+2 (c 1, H_2O)					0.23	0
H-Lys-γ-Abu-OH·HCl (12)	100	oily						0.31	0

Table II. Yields and Analytical Data of Synthetic Peptides in Group II

compd	yield, %	mp, °C	$[\alpha]_D^{23}$, deg (solvent)	formula	found (calcd), % C	H	N	R_{f1}	R_{f2}
Cbz-Gly-Orn(δ-Cbz)-OBzl	68	88	−13 (c 1, MeOH)	$C_{30}H_{33}O_7N_3$	65.70 (65.80)	6.25 (6.07)	7.56 (7.67)	0.97	0.94
Cbz-β-Ala-Orn(δ-Cbz)-OBzl	77	113	−17 (c 1, MeOH)	$C_{31}H_{35}O_7N_3$	66.13 (66.29)	6.36 (6.28)	7.50 (7.48)	0.96	0.77
Cbz-γ-Abu-Orn(δ-Cbz)-OBzl	81	128–129	−16 (c 1, MeOH)	$C_{32}H_{37}O_7N_3$	66.83 (66.76)	6.55 (6.48)	7.37 (7.30)	0.97	0.91
Cbz-Gly-Lys(ε-Cbz)-OBzl	68	111	−14 (c 1, MeOH)	$C_{31}H_{35}O_7N_3$	66.01 (66.29)	6.11 (6.28)	7.63 (7.48)	0.96	0.93
Cbz-β-Ala-Lys(ε-Cbz)-OBzl	66	121	−15 (c 1, MeOH)	$C_{32}H_{37}O_7N_3$	66.91 (66.76)	6.50 (6.48)	7.56 (7.30)	0.96	0.77
Cbz-γ-Abu-Lys(ε-Cbz)-OBzl	65	115	−16 (c 1, MeOH)	$C_{33}H_{39}O_7N_3$	66.92 (67.21)	6.63 (6.67)	7.31 (7.13)	0.99	0.89
H-Gly-Orn-OH·HCl (13)	91	hygroscopic						0.10	0
H-β-Ala-Orn-OH·HCl (14)	77	hygroscopic						0.06	0
H-γ-Abu-Orn-OH·HCl (15)	93	hygroscopic						0.11	0
H-Gly-Lys-OH·HCl (16)	44	hygroscopic						0.10	0
H-β-Ala-Lys-OH·HCl (17)	75	hygroscopic						0.12	0
H-γ-Abu-Lys-OH·HCl (18)	100	oily						0.08	0

Syntheses of Group II. The peptides of group II were synthesized on as equal scale and in the same way as group I. The physical properties of synthetic peptides, and their derivatives, of group II are listed in Table II.

Syntheses of Group III. The peptides of group III were synthesized by the active ester method. Dibenzyloxycarbonyl amino acid succinimide ester and taurine (2-aminoethanesulfonic acid) were coupled to yield the corresponding protected dipeptide derivative. The protecting groups of the intermediate were removed by catalytic hydrogenation in acetic acid solution. The product was treated with HCl–dioxane and obtained in the form of hydrochloride.

L-(*1,2-Diaminopropionyl*)*taurine Hydrochloride* **(19).** Cbz-L-A_2Pr^3 (β-Cbz)-OH·DCHA (5.54 g, 10 mmol) was dissolved in ethyl acetate (40 mL), and 1 M sulfuric acid (10 mL) was added to the mixture with stirring. The organic layer was washed with water and dried over anhydrous sodium sulfate. The solution was concentrated to dryness in vacuo. The oily residue and *N*-hydroxylsuccinimide (2.30 g, 20 mmol) were dissolved in acetonitrile (40 mL). Dicyclohexylcarbodiimide (4.12 g, 20 mmol) was added to the mixture at 0 °C. After 1 h, the reaction mixture was allowed to stand at 5 °C with stirring overnight. *N,N*-Dicyclohexylurea was filtered off and the filtrate was evaporated in vacuo. The oily residue was

Table III. Yields and Analytical Data of Amino Acid and Peptide Derivatives in Group III

compd	yield, %	mp, °C	$[\alpha]_D^{23}$, deg (solvent)	R_{f1}	R_{f2}
Cbz-A_2Pr^3(β-Cbz)-ONSu	78	85–87	−26 (c 1, DMF)	0.91	0.65
Cbz-A_2bu(γ-Cbz)-ONSu	82	80–83	−25 (c 1, DMF)	0.92	0.67
Cbz-Orn(δ-Cbz)-ONSu	75	99–101	−8 (c 1, DMF)	0.96	0.77
Cbz-Lys(ϵ-Cbz)-ONSu	80	107–109	−15 (c 1, DMF)	0.92	0.76
Cbz-A_2Pr^3(β-Cbz)-Tau	65	155–157	−12 (c 1, H_2O)	0.81	0.17
Cbz-A_2bu(γ-Cbz)-Tau	65	145–147	−18 (c 1, H_2O)	0.76	0.10
Cbz-Orn(δ-Cbz)-Tau	100	167	−11 (c 1, H_2O)	0.65	0.14
Cbz-Lys(ϵ-Cbz)-Tau	60	139	−11 (c 1, H_2O)	0.83	0.21
H-A_2Pr^3-Tau·HCl (19)	74	hygroscopic	+3 (c 1, H_2O)	0.13	0
H-A_2bu-Tau·HCl (20)	73	hygroscopic	+9 (c 1, H_2O)	0.15	0
H-Orn-Tau·HCl (21)	100	hygroscopic	+6 (c 1, H_2O)	0.14	0
H-Lys-Tau·HCl (22)	85	hygroscopic	+10 (c 1, H_2O)	0.19	0

crystallized by the aid of ethyl acetate to give a crude product. It was recrystallized from hot ethyl acetate to give pure Cbz-L-A_2Pr^3 (β-Cbz)-ONSu.

To a solution of Cbz-L-A_2Pr^3 (β-Cbz)-ONSu (1.41 g, 3 mmol) in tetrahydrofuran (10 mL), a solution of taurine (0.50 g, 4 mmol) and triethylamine (0.56 mL, 4 mmol) in water (10 mL) was added. The reaction mixture was allowed to stand at room temperature for a day and then was evaporated in vacuo. The aqueous layer was acidified with 6 M HCl and then extracted with ethyl acetate. The organic layer was washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate for 3 h. The filtrate was evaporated in vacuo, and the oily residue was crystallized by the aid of ether to give Cbz-L-A_2Pr^3 (β-Cbz)-Tau.

A solution of Cbz-L-A_2Pr^3 (β-Cbz)-Tau (0.53 g, 1.1 mmol) in acetic acid (5 mL) was hydrogenated in the presence of palladium black at room temperature for 1.5 h. The catalyst was removed by filtration and the filtrate was evaporated in vacuo, and then the residue was solidified by the aid of 5.6 M HCl–dioxane (0.20 mL, 1.1 mmol) and ethanol. The final product was obtained as a hygroscopic solid.

Compounds **20–22** were obtained by the same method as described above. The physical properties are listed in Table III.

RESULTS AND DISCUSSION

Most of synthesized dipeptides in group I had a pronounced umami taste. Some of them exhibited both umami and salty tastes. In addition to H-L-Orn-Gly-OH·HCl (7) and H-L-Lys-Gly-OH·HCl (10), H-L-Orn-β-Ala-OH·HCl (8) and H-L-Orn-γ-Abu-OH·HCl (9) exhibited a salty taste twice as strong as that of NaCl. There was no disagreement among the four panelists as to the above-mentioned salty taste, indicating the high reliability of the results in Table IV. It is suggested that exhibition of the umami taste requires that the strict length of the dipeptide skeleton be maintained (m = 1) as shown in Figure 2. It is not, however, affected by the side chain length of the basic amino acid residue. The salty taste requires just the opposite. The salty taste was also observed in sulfonyl salts and p-toluenesulfonyl salts; however, the latter was accompanied by a bitter taste.

Table IV. Sensory Analysis of Synthesized Dipeptides

compd[a]	taste	TV,[b] mM	quality[c] salt	quality[c] umami
group I				
A_2Pr^3-Gly·HCl (1)	umami	2.44	0	2
A_2Pr^3-β-Ala·HCl (2)	umami	6.25	0	1
A_2Pr^3-γ-Abu·HCl (3)	flat		0	0
A_2bu-Gly·HCl (4)	umami	2.36	0	4
A_2bu-β-Ala·HCl (5)	umami	1.56	0	3
$A_2$by-γ-Abu·HCl (6)	salty(weak)	1.56	2	0
Orn-Gly·HCl (7)	salty/umami	1.62	3	4
Orn-β-Ala·HCl (8)	salty	1.25	4	1
Orn-γ-Abu·HCl (9)	salty	1.40	4	1
Lys-Gly·HCl (10)	salty/umami	1.22	3	4
Lys-β-Ala·HCl (11)	umami	6.25	1	3
Lys-γ-Abu·HCl (12)	umami		0	1
group II				
Gly-Orn·HCl (13)	sour/sweet	5.48	0	0
β-Ala-Orn·HCl (14)	sour/sweet	4.82	0	0
γ-Abu-Orn·HCl (15)	sweet/sour	2.89	0	0
Gly-Lys·HCl (16)	sour/sweet	5.48	0	0
β-Ala-Lys·HCl (17)	sweet/sour	4.68	0	0
γ-Abu-Lys·HCl (18)	sweet/sour	1.56	0	0
group III				
A_2Pr^3-Tau·HCl (19)	sour/sweet	5.50	0	0
A_2bu-Tau·HCl (20)	sour/salty	1.56	1	0
Orn-Tau·HCl (21)	salty	3.68	5	0
Lys-Tau·HCl (22)	salty	5.18	5	0
NaCl	salty	3.12	5	0
MSG	umami	1.56	0	5

[a] The abbreviations recommended by the IUPAC-IUB Commission of Biochemical Nomenclature (1972) have been used. Amino acid symbols (except glycine, β-alanine, and γ-aminobutylic acid) denote L configuration. [b] TV = threshold value. [c] Quality of the sample was compared with that of NaCl or MSG solution. It was evaluated on a score of 0–5 wherein 5 was judged to be equivalent to the reference (NaCl or MSG) solution. The indicated results are consensus scores by the four panelists.

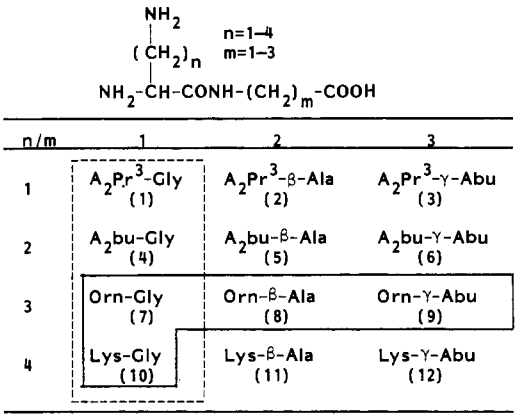

Figure 2. Distribution of salty and umami taste in group I. A solid line indicates salty peptides, and a dashed line indicates umami peptides.

The results of group II were interesting since several dipeptides were sweet with sour taste. Among them, H-γ-Abu-L-Lys-OH·HCl (18) exhibited a taste appreciably sweeter than that of sucrose. From the results of group I and group II, it is supposed that the distance between the amino group of the branched chain and C-terminal carboxyl group is important for governing both the umami and salty tastes.

Other analogues, in which the carboxyl group of β-alanine was substituted by the sulfonyl group, were also synthesized. During the sensory tests, H-L-Orn-Tau·HCl (21) and H-L-Lys-Tau·HCl (22) were discovered to possess a savory salty taste the same as that of NaCl. These salty tastes surpassed that of H-L-Orn-β-Ala-OH·HCl (8). It is

suggested that the salty taste quality is influenced by the degree of dissociation, when one compared the sulfonyl group with the carboxyl group.

Some of these salty and umami peptides must be safety tasted prior to human consumption, as they become amino acids by hydrolyzation, which are natural components. In view of the above, we expect that these peptides, which contain no sodium ion in the molecule, will prove valuable as a new type of seasoning, replacing NaCl and MSG (which contain a sodium ion) for diabetics and hypertensives.

Registry No. 1, 90970-28-8; 2, 90970-29-9; 3, 90970-30-2; 4, 91049-41-1; 5, 90970-31-3; 6, 90970-32-4; Cbz-A_2Pr^3-(β-Cbz)-β-Ala-OBzl, 90970-33-5; 8, 90970-63-1; 9, 90970-34-6; Cbz-A_2bu-(γ-Cbz)-β-Ala-OBzl, 40719-58-2; 11, 90970-35-7; 12, 90970-36-8; 13, 90970-37-9; 14, 90970-38-0; 15, 90970-39-1; 16, 31461-63-9; 17, 90970-40-4; 18, 90970-41-5; 19, 90970-42-6; 20, 90970-43-7; 21, 90970-64-2; 22, 90970-44-8; MSG, 142-47-2; Cbz-L-A_2Pr^3(β-Cbz)-OH·DCHA, 91049-42-2; H-Gly-OBzl·TsOH, 1738-76-7; Cbz-A_2Pr^3(β-Cbz)-Gly-OBzl, 90970-45-9; Cbz-A_2Pr^3(B-Cbz)-β-Ala-OBzl, 90970-46-0; Cbz-A_2Pr^3(β-Cbz)-γ-Abu-OBzl, 90970-47-1; Cbz-A_2bu(γ-Cbz)-Gly-OBzl, 90990-57-1; Cbz-A_2bu(γ-Cbz)-β-Ala-OBzl, 90970-48-2; Cbz-A_2bu(γ-Cbz)-γ-Abu-OBzl, 90970-49-3; Cbz-Orn(δ-Cbz)-Gly-OBzl, 90970-50-6; Cbz-Orn(δ-Cbz)-β-Ala-OBzl, 90970-51-7; Cbz-Orn(δ-Cbz)-γ-Abu-OBzl, 90970-52-8; Cbz-Lys-(ε-Cbz)-Gly-OBzl, 90970-53-9; Cbz-Lys(ε-Cbz-β-Ala-OBzl, 90990-58-2; Cbz-Lys-(ε-Cbz)-γ-Abu-OBzl, 90970-54-0; Cbz-Gly-Orn(δ-Cbz)-OBzl, 90970-55-1; Cbz-β-Ala-Orn(δ-Cbz)-OBzl, 90970-56-2; Cbz-γ-Abu-Orn(δ-Cbz)-OBzl, 90970-57-3; Cbz-Gly-Lys(ε-Cbz)-OBzl, 6366-71-8; Cbz-β-Ala-Lys(ε-Cbz)-OBzl, 90970-58-4; Cbz-γ-Abu-Lys(ε-Cbz)-OBzl, 90970-59-5; Cbz-A_2Pr^3(β-Cbz)-ONSu, 65581-27-3; Cbz-A_2bu(γ-Cbz)-ONSu, 90970-60-8; Cbz-Orn(δ-Cbz)-ONSu, 90970-61-9; Cbz-Lys(ε-Cbz)-ONSu, 21160-83-8; Cbz-A_2Pr^3(β-Cbz)-Tau, 90970-62-0; Cbz-A_2bu(γ-Cbz)-Tau, 90990-59-3; Cbz-Orn(δ-Cbz)-Tau, 90990-60-6; Cbz-Lys(ε-Cbz)-Tau, 90990-61-7.

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