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The common pure amino acids have the following taste properties near neutrality: no taste at all or a barely perceptible taste (D-Ala, D- and L-Arg, D- and L-Asp, D-Glu, L-His, D- and L-Ile, D- and L-Lys, D- and L-Pro, D- and L-Ser, D- and L-Thr, D- and L-Val), sweet taste (in order of decreasing sweetness: D-Try, D-His, D-Phe, D-Tyr, D-Leu, L-Ala, Gly), bitter taste (in order of decreasing bitterness: L-Try, L-Phe, L-Tyr, L-Leu), and sulfurous taste (D- and L-CySH and D- and L-Met). L-Glutamic

The many important biological functions that amino acids, peptides, and proteins fulfill has focused research in the past decades on the physiological role of these compounds. Recently, the less fundamental aspects such as taste and flavor have become of interest. The present review is concerned with the direct contributions of amino acids, peptides, and proteins to the flavor of foods; their importance as flavor precursors is not considered.

The taste qualities of the pure substances will be considered first. The literature on this subject is controversial (Berg, 1953; Crocker, 1948; Ferguson and Lawrence, 1958; Galvin, 1948; Lawrence and Ferguson, 1959; Meister, 1957; Stone, 1967). This is probably because pure D- and L-amino acids were not readily available in the past, that differences in taste between the optical isomers were often not duly considered, and that chemical impurities often conveyed agreeable "hydrolysate flavors" to the test substances. Moreover, many taste tests were conducted only on a qualitative basis and at varying concentrations.

In Table I, results are presented from statistical taste tests conducted with a selected panel of eight to 12 people, using pure L- and D-amino acids (Solms *et al.*, 1965). The amino acids with taste properties were compared with standard substances having the same taste quality and known taste intensities. All taste tests were conducted at the same fixed concentration of amino acid(0.3%), although it is known that taste quality may vary with concentration. Experimental details are reported elsewhere (Solms *et al.*, 1965).

Three groups of amino acids can be established. Group 1 consists of amino acids whose L- and D-enantiomorphs have no taste at all, or only a barely perceptible taste. Group 2 consists of amino acids with complex taste sensations, which are difficult to evaluate in the pure state. This group contains the unique L-glutamic acid, known for its flavor-enhancing properties in suitable mixtures (Neukom, 1956; Oeda, 1963; Solms, 1967a, 1967b), and the sulfur-containing amino acids. The latter probably form decomposition products, which are responsible for their sulfurous taste. Group 3 comprises amino acids with distinctive tastes, either bitter or sweet, which were comacid has a unique taste-potentiating property; a similar effect has been reported for tricholomic acid and ibotenic acid. Pure peptides have been investigated to a lesser extent. Examples are presented of peptides with bitter and other taste sensations. Proteins have been found to provide tactual and astringent effects. The contributions of these substances to the flavor of food products often exceed the taste properties of the pure compounds.

pared quantitatively with caffeine and sucrose solutions, respectively. The taste intensities of the amino acids in this group, especially those of the aromatic amino acids, are noteworthy. L-Tryptophan is approximately half as bitter as caffeine; D-tryptophan is 35 times sweeter than sucrose. L- and D-phenylalanine and L- and D-tyrosine have similar but less intense taste qualities. Alanine and histidine form a special subgroup, with one isomer flat in taste, the other sweet. Alanine is the only amino acid tested with a truly sweet-tasting L-enantiomorph. Glycine, named for its sweet taste, has the lowest relative sweetness of the amino acids in this group. Free aromatic L-amino acids occur in relatively high concentrations. together with other amino acids, in oriental food preparations (Murata et al., 1967; Yokotsuka, 1960), and in many cheese varieties, especially in ripe ones (Hintz et al., 1956; Kosikowski and Dahlberg, 1954; Ritter et al., 1966), and may directly influence the taste or off-taste of these foods.

Two amino acids, which have not been tested, are ibotenic acid and tricholomic acid (Solms, 1967b, Takemoto, 1966). They are reported to exert flavor enhancing properties similar to glutamic acid, with much higher intensity.

Finally, a compound derived from glutamic acid, pyrrolidone-carboxylic acid, is claimed to possess a disagreeable bitter "off-taste" (Mahdi *et al.*, 1961; Shallenberger and Moyer, 1958).

Much less is known about the taste of peptides, but there are probably no simple relations to the amino acids. The peptide L-glycyl-L-tryptophan, for example, is not bitter in taste, although it contains L-tryptophan (Solms, 1968b). It is a well-known observation that bitter tasting products are formed during enzymatic hydrolysis of proteins. This apparently is due to the formation of bitter tasting peptides, especially phosphopeptides--e.g., in cheese production (Harwalkar, 1967; Murray and Baker, 1952; Raadsveld, 1953; Stone and Naff, 1967). Although many peptides have been isolated from enzymatic protein hydrolyzates and from cheese, detailed studies of their structures combined with taste evaluations have not as yet been published. Thus far only one peptide with a bitter taste has been examined in detail, and it contains the following amino acids: leucine, glutamic acid, and valine (Carr et al., 1956).

Many peptides have been isolated from plants and animals, but have not been tested for their taste properties. At least two peptides, γ -L-glutamyl-S-(prop-1-enyl)-L-

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	Taste		
Amino Acid	L-Form	D-Form	
Group 1. Amino Acids w	ithout Taste		
Arginine	Flat	Sl. sweet (D, L)	
Aspartic acid	Flat	Flat	
Isoleucine	Flat	Flat	
Lysine	Flat	Flat	
Proline	Flat, sl. sweet	Flat (D, L)	
Serine	Flat	Flat	
Threonine	Flat	Flat	
Valine	Flat	Flat	
Glutamic acid	• • •	Flat	
Group 2. Amino Acids w	ith Varying Tastes		
Cysteine	Sulfurous	Sulfurous (D, L)	
Glutamic acid	Unique, "glutamate"		
Methionine	Sulfurous, meaty	Sulfurous, meaty	
	Sl. sweet	Sl. sweet	
Group 3. Amino Acids w (as compared with solution	ith Bitter or Sweet Tastes ons of caffeine or sucrose)		
Alanine	Sweet, 0.54% sucrose	Flat	
Histidine	Flat	Sweet, 2.23% sucro	
Leucine	Bitter, 0.011% caffeine	Sweet, 1.30% sucro	
Phenylalanine	Bitter, 0.069% caffeine	Sweet, 2.20% sucro	
Tryptophan	Bitter, 0.133% caffeine	Sweet, 11.00% sucro	
Tyrosine ^c	Bitter, 0.017% caffeine	Sweet, 1.65% sucro	
Glycine	Sweet, 0.4	5% sucrose	

Table I. Taste of Amino Acids in 0.3% Aqueous Solutions^{a,b}

^c Due to the low solubility of tyrosine, the taste tests were conducted at elevated temperatures.

cysteine isolated from chives, and γ -L-glutamyl-S-(prop-1-enyl)-L-cysteine sulfoxide isolated from onions, were evaluated for taste, and they exhibited a characteristic biting taste sensation (Virtanen, 1965, 1968). An agreeable taste has been described for anserine (Jones, 1961). Certain flavor-enhancing properties have been assigned to calcium pantothenate (Dixon, 1968) and to several copolypeptides containing glutamic acid, aspartic acid, lysine, and ornithine (Kyowa Hakko Kogyo Co., 1965, 1967a, 1967b). For many years it has been claimed that glutathione is responsible for meaty taste (Bouthilet, 1951), but this is probably not correct.

It is generally accepted that proteins exert no taste activity; however, they contribute to flavor indirectly, with tactile and similar effects. This is especially true for protein-rich foods like milk, milk products, and meat (Matz. 1962). Astringency should also be mentioned as a direct contribution of these substances to taste (Josephson et al., 1967).

In food preparations the contribution of amino acids and peptides to the flavor of the product often exceeds the taste properties of the pure compounds themselves, because of the phenomena of taste interactions, like synergism and potentiation (Amerine et al., 1965; Solms, 1967a, 1967b). The best known example is L-glutamic acid, which exerts a pronounced taste-improving effect in appropriate mixtures, or in foods, due to flavor potentiation. Other compounds are much less effective, and must be regarded as secondary substances, which provide a background for a flavor potentiator (Hashimoto, 1965).

To assess the taste contribution of these substances, they must be tested in their natural environment. The first systematic approach, in this regard, has been described by Mulder (1952) with the "components balance theory" of cheese flavor. The theory states that flavor is not related to single compounds, but to a mixture of volatile and nonvolatile compounds, including amino acids, which must occur in a certain specific balance. The theory has been examined and confirmed by Silverman and Kosikowski (1953) and by Kosikowski and Mocquot (1958). Hashimoto (1965) developed a similar approach for evaluating the flavor of meat and fish; Craske and Reuter (1965) applied a somewhat different technique for mushroom flavor. The difficulties of the method were recently discussed for cheese flavor (Day et al., 1957). They are mainly due to the fact that the amino acids do not impart a typical flavor as such, but appear to function by providing a general background on which the typical flavor notes are superimposed. The character of the background depends on the qualitative and quantitative composition of the mixture (Dylanyan et al., 1966).

The amino acid fraction of Swiss cheese is an interesting example. Only a combination of the amino acids Lproline (6000 p.p.m.), glycine (1600 p.p.m.), L-serine (1950 p.p.m.), L-threonine (1950 p.p.m.), L-aspartic acid (2500 p.p.m.), L-glutamic acid (3000 p.p.m.), L-cysteine (760 p.p.m.), L-tryptophan (2200 p.p.m.), L-histidine (3700 p.p.m.), and L-lysine (2200 p.p.m.), together with selected free fatty acids and selected volatiles, gave reconstituted Swiss cheese flavor (Langler et al., 1967).

Other amino acid mixtures of specific qualitative and quantitative composition, which contribute to basic flavor notes, are reported for onions (Take and Otsuka, 1968), crabmeat (Take et al., 1968), fish and fish extracts (Hashimoto, 1965), soy sauce and other seasonings (Kikkoman Shoyu Ltd., 1967, 1968), and chicken and meat broth (Ajinomoto Co., 1967; Kazeniac, 1961). In the latter, hydroxyproline seems to be of special interest (Kawano, 1962).

The importance of free amino acids in the flavor of potatoes has been investigated in some detail (Solms et al., 1969). The nonvolatile extracts of boiled potatoes con-

Table II.	Proposed	Integrated	Flavor	Picture
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Total flavor sensation	Volatile fraction	Low boiling compds. High boiling compds.
	Nonvolatile fraction	Flavor potentiators, synergists Compds. with taste and tactile effects

tain at least three interesting fractions-namely, (I) nucleotides (adenosine-5'-phosphate, cytidine-5'-phosphate, guanosine-5'-phosphate, guanosine-2',3'-phosphate, uridine-5'-phosphate, uridine-2',3'-phosphate), (II) L-glutamic acid and (III) other free amino acids (L-Ala, L-Arg, L-Asp, Gly, L-His, L-Ile, L-Leu, L-Lys, L-Met, L-Pro. L-Phe, L-Ser, L-Thr, L-Try, L-Tyr, L-Val). A stepwise recombination of these fractions with pure substances at the proper concentrations gives a distinct stepwise increase in taste quality, as judged by panel comparison tests. The final, total mixture has practically no odor but has a distinct basic potato taste. However, a fully-reconstituted potato flavor is not achieved, because other nonvolatiles and the whole volatile flavor fraction are missing.

Amino acids, peptides, and proteins seem to have a place in an integrated flavor picture. Possible flavor relations for various compounds were recently proposed for meat flavor (Solms, 1968a). Other flavors are composed in a similar fashion of four groups of substances, with close interrelationships, each of which should occur in a specific balance to give an over-all flavor sensation (Table II). Amino acids, peptides, and proteins are located at the base of this scheme, providing taste and tactile effects; certain compounds act as flavor potentiators and synergists, and act as a bridge between the nonvolatile and volatile fractions. The volatile fractions are located at the top of the scheme and contribute important odor effects described elsewhere in the flavor literature. All groups together then form the integrated flavor picture.

REFERENCES

- Ajinomoto Co., Inc., French Patent **1,474,613** (Feb. 13, 1967). Amerine, M. A., Pangborn, R. M., Roessler, E. B., "Principles of Sensory Evaluation of Food," Academic Press, New York, 1965.
- Berg, C. P., Physiol. Rev. 33, 145 (1953)
- Bouthilet, R. J., Food Res. 16, 201 (1951). Carr, J. W., Loughheed, T. C., Baker, B. E., J. Sci. Food Agr. 7, 629 (1956).
- Craske, J. D., Reuter, F. H., J. Sci. Food Agr. 16, 243 (1965). Crocker, E. C., "Monosodium Glutamate," W. F. Dove, Ed.,
- p. 25, Food and Container Institute. Chicago, 1948.
 Day, E. A., "Symposium on Foods, The Chemistry and Physiology of Flavors," H. W. Schultz, E. A. Day, C. M. Libbey, Eds., p. 331, Avi Pub. Co., Inc., Westport, Conn., 1967.
 Dixon, M. P., Ret, Nutr. Food Sci. 1968, 6 (10).
- Dylanyan, Z., Agababyan, A., Ioanissyan, J., Zakharyan, L., XVII. Intern. Dairy Congress, Sect. D, Cheese, p. 301, Munich, 1966.

- Ferguson, L. N., Lawrence, L. W., *J. Chem. Educ.* **35**, 436 (1958). Galvin, S. L., "Monosodium Glutamate," W. F. Dove, Ed., p. 39, Food and Container Institute, Chicago, 1948.
- Jawalkar, V. R., J. Dairy Sci. 50, 956 (1967).
 Hashimoto, V., "The Technology of Fish Utilization," R. Kreuzer, Ed., p. 57, Fishing News Ltd., London, 1965.
 Hintz, P. C., Slatter, W. L., Harper, W. J., J. Dairy Sci. 39, 235
- (1956).
 Jones, N. R., "Flavor Chemistry Symposium," p. 61, Campbell Soup Co., Camden, N. J., 1961.
 P. V. Thomas, E. L., Morr, C. V., Coulter, T.,
- Josephson, R. V., Thomas, E. L., Morr, C. V., Coulter. T., J. Dairy Sci. 50, 1376 (1967).
- Kawano, Y., Japanese Patent Appl. **56,792/62** (Dec. 24, 1962). Kazeniac, S. J., "Flavor Chemistry Symposium," p 37, Camp-
- bell Soup Co., Camden, N. J., 1961. Kikkoman Shoyu Ltd., French Patent **1,469,024** (Jan. 2. 1967). Kikkoman Shoyu Co., *CA* **68**, 28635 (1968).
- Kosikowski, F. V., Dahlberg, A. C., J. Dairy Sci. 37, 167 (1954).
- Kosikowski, F. C., Mocquot, G., "Progrès de la technologie du fromage," Etudes Agricoles, FAO, No. 38, p. 151, Rome, 1958.
- Kyowa Hakko Kogyo Co., Ltd., French Patent 1,413,451 (Aug. 30, 1965).
- Kyowa Hakko Kogyo Co., Ltd., British Patent 1,068,478 (Apr. 4. 1967a).
- Kyowa Hakko Kogyo Co., Ltd., British Patent 1,083,189 (1967b). Langler, J. E., Libbey, L. M., Day, E. A., J. AGR. FOOD CHEM.
- 15, 386 (1967). Lawrence, A. R., Ferguson, L. N., Nature 183, 1469 (1959).
- Mahdi, A. A., Rice, A. C., Weckel, K. G., J. AGR. FOOD CHEM. 9.143.(1961)
- Matsuda, I., Shiga, A., Kanemitsu, A., U. S. Patent 3,340,069 (1968).
- Matz, S. A., "Food Texture," Avi Pub. Co., Westport, Conn., 1962.
- Meister, A., "Biochemistry of the Amino Acids," Academic Press, New York, 1957.
- Mulder, H., Neth. Milk Dairy J. 6 (2), 157 (1952).
- Murata, K., Ikehata, H., Miyamoto, T., J. Food Sci. 32, 580 (1967).
- Murray, T. K., Baker, B. E., J. Sci. Food Agr. 3, 470 (1952).
- Nullay, T. K., Bakel, B. E., J. Sci. Tool Agr. 5, 410 (1952).
 Neukom, H., Chimia 10, 203 (1956).
 Oeda, H., "Monosodium Glutamate," in "Encyclopedia of Chemical Technology," 2nd ed., 2, 198 (1963).
 Raadsveld, C. W., Proc. XIII Intern. Dairy Congr. 2, 676 (1953).
 Ritter, W., Schilt, P., Lowe, A., XVII Intern. Dairy Congr., Sect. D, Cheese, p. 269 (1966).
 Shallenberger, R. S., Moyer, J. C., J. AGR. FOOD CHEM. 6, 604 (1958).

- 604 (1958).
- Silverman, G. J., Kosikowski, F. V., J. Dairy Sci. 36, 574 (1953). Solms, J. "Aroma- und Geschmacksstoffe in Lebensmitteln," J. Solms, H. Neukom, Eds., p. 199, Forster Verlag, Zurich, 1967a.
- Solms, J., Chimia 21, 169 (1967b)
- Solms, J., Fleischwirtschaft 48, 287 (1968a).
- Solms, J., unpublished observation, 1968b
- Solms, J., Signer, V., Buri, R., Lebensm.-Wiss. Technol., to be published (1969).
- Solms, J., Vuataz, L., Egli, R. H., *Experientia* **21**, 692 (1965). Stone, H., "Olfaction and Taste II," T. Hayashi, Ed., p. 289,
- Pergamon Press, Oxford, 1967. Stone, W. K., Naff, D. M., J. Dairy Sci. 50, 1497 (1967).
- Take, T., Otsuka, H., *CA* **68**, 28563 (1968). Take, T., Yoshimura, Y., Otsuka, H., *CA* **68**, 28562 (1968).
- Takemoto, T., Japan. Med. Gaz. 3 (5), 5 (1966). Virtanen, A. I., Phytochemistry 4, 207 (1965).
- Virtanen, A. I., Biochemical Research Institute, Helsinki, Finland, personal communication, 1968
- Yokotsuka, T., Advan. Food Res. 10, 75 (1960).

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