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MONOSODIUM GLUTAMATE

a symposium

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Flavor and Acceptability of
MONOSODIUM GLUTAMATE

Proceedings of the Symposium
March 4, 1948
The Stevens Hotel, Chicago, Illinois

Sponsored Jointly by

The Quartermaster Food and Container Institute for the Armed Forces, and Associates, Food and Container Institute
1849 West Pershing Road, Chicago 9, Ill.

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The First Symposium On Monosodium Glutamate

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Food Acceptance Branch
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1849 West Pershing Road, Chicago 9, Illinois

We are gathered here from all parts of the country to discuss one chemical substance—monosodium glutamate. The production, formulation and consumption of that one chemical substance, derived from food and returned to the food for the purpose of enhancing acceptability, raises numerous problems in many fields of science and applied science. To discuss these problems is why we are here today.

Without doubt, life could go on in hit or miss fashion but not so successfully as it does when we plan, organize, and streamline our affairs and frequently re-orient ourselves to each other and to the results of progress made to date. This is especially true with regard to the subject of monosodium glutamate. Continued refinement in production methods, for instance, produces a more highly purified substance. Successive purification in turn alters the organoleptic properties to the extent that the glutamate loses some of its own intrinsic flavors in the process of washing out the "impurities," but extends its abilities as an enhancer of other natural flavors of foods with which it is combined. By the same token monosodium glutamate moves out of the category of an artificial flavoring which it might otherwise simulate, into the category of a seasoner or condiment in its own right.

During this process of refinement it shifts up, as it were, from a lower social class to a higher order, and yet it must continue to rub elbows with its poorer relatives—the protein hydrolysates of broad flavor effects.

In many biological processes the purification of any one essential substance activates otherwise quiescent or slow-moving organic changes. With respect to monosodium glutamate this activity may be expressed either as a reaction in food with which it is combined, packaged and stored, or as a promoter in itself, of physiological, sensory or organic changes in the consumer.

The foregoing statement epitomizes what will be attempted here at this Symposium. In bringing together specialists who have worked upon many phases of an ever-expanding reaction system in which monosodium glutamate participates, we planned to have each speaker treat some special phase of this story of glutamate as the day's program moves through sections on History, Production Methods, Uses, Formu-

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lation in Practice, Chemical Nature and Relationships, Psychophysiological Aspects, and Value in Medical Pharmacological Practices.

Military Interest

Army food acceptance research on monosodium glutamate has been concerned to date with psychophysical studies carried on by Dr. Rosaltha Sanders in the Physiology Section of the Food Acceptance Branch. In brief, the studies are basic to a better understanding of the chemistry and physiology of taste and flavor. For example, when we add to the existing knowledge on the nature of the primary tastes, information on the variations effected by substances such as monosodium glutamate which stimulate several primary tastes including other and secondary effects, we increase fundamental research in a direction useful to commodity and ration development.

Tests have also been made on the effect of glutamate on the flavor of common canned vegetables as acceptance studies by Miss Louise Seiter in the Technology Section of the Food Acceptance Branch.

An extension of tests on acceptability into actual field conditions was also provided the writer when participating in the Arctic Field Trials during February 1948. Among the four groups of test subjects who were living in tents in the Arctic winter, under conditions simulating crash landing, one group was provided with the Parachute Emergency ration as the only means of subsistence for a 10-day period. The one food item besides the chocolate bar and bouillon cube was a cheese and cracker bar.

During the first two days, this cheese and cracker bar was rated high in acceptability. By the third and fourth day acceptability had declined to moderate; by the sixth day the item was being refused as disliked; on the seventh to tenth day it was highly disliked, and the men preferred to go into a state of semi-starvation rather than eat the same monotonously limited food day after day. This evidence neatly disposes of the commonly held assumption that a hungry man will eat just anything. In addition to this record showing that acceptability is one of the chief military characteristics of foods and rations, the record of the responses of the subjects to this diet is important to us today. As monotony set in, usually by the third or fourth day, the subjects frequently inquired: "Can't you get other flavors into this bar?" "Why not add a meaty flavor, a chicken flavor, fruit and another cereal?" This response may represent one of the answers to a military feeding problem, and monosodium glutamate and the protein hydrolysates may prove in their ability to enhance flavor a means of mitigating monotony of diet.

The success of this adventure will be reflected only in future trends.

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I would like, however, to quote from one of the numerous responses received since the Symposium:

"The results of this Symposium will prove to be of much value not only to the monosodium glutamate producing industry but to a much greater extent to the consuming industry. I sincerely hope that ways and means may be devised whereby this movement, which you have initiated, may be continued with increasing emphasis."

MORNING SESSION

Introductory Remarks

COLONEL CHARLES S. LAWRENCE,
Commanding Officer
Quartermaster Food and Container Institute
for the Armed Forces
1849 West Pershing Road, Chicago 9, Illinois

It is with both pleasure and satisfaction that I welcome you this morning and call to order this symposium on the flavor and acceptability of monosodium glutamate. The symposium is an event that we have all been awaiting with great expectations, and I am confident that in the capable hands of our distinguished participants, we shall not be disappointed in the results. That phrase "great expectations" has, of course, an ominous ring. I once knew a man who inscribed in a cook-book that he was giving to his wife on their first wedding anniversary "To Louise from John—with great expectations." The phrase backfired, as bright remarks sometimes do, for his wife read into it a vague dissatisfaction with her past culinary efforts and like the woman scorned she was in a considerable fury.

But our speakers, our topics, and our keen interest in this curious substance, monosodium glutamate, permit us to expect a profitable symposium today. We shall learn things about the production of glutamate, its use as a flavoring agent in various food products, its relation to the browning reaction, the pharmacology of glutamic acid, and the thresholds of perception of glutamate. You will agree, I am sure, that these topics pretty well encircle the game we are after, and there is little reason to doubt that we shall flush some interesting things to shoot at in the course of the day.

On behalf of the Associates and the Institute, let me express our appreciation for your attendance today and our thanks for the fine cooperation we have had from you in making this symposium possible.

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History of Glutamate Manufacture

ALBERT E. MARSHALL
President, Rumford Chemical Works
Rumford, R. I.

(Presented by Mr. Bishop in the absence of Dr. Marshall)

Author's abstract

The flavor-enhancing material, monosodium glutamate, is not produced commercially by chemical synthesis, but by hydrolysis of proteins, usually vegetable in origin.

Its chemical composition was determined eighty years ago, but its flavor-building properties remained unnoticed until 1908 when Dr. K. Ikeda, Tokyo University, found that an edible seawood, used in Japanese cookery, contained glutamate.

Shortly after this discovery manufacture of glutamate by acid hydrolysis was undertaken in Japan, the raw material employed being wheat gluten, which, later on, was supplemented by soya bean protein.

Use of glutamate as a pleasing modifier of the customary monotonous diets of the Orient, resulted, within a decade, in its substantial production in Japan, also its manufacture on a smaller scale in China.

Brought from the Orient to the United States in the mid-1920's, possibilities of domestic manufacture were studied and a project based on hydrolysis of wheat gluten undertaken. At about the same time other sources of glutamate were investigated, and in 1926 a plant was built for its extraction from beet sugar residues. Projected on an acid hydrolysis step, the operations were unsuccessful. After ten years of research and pilot plant experiments, despite literature statements that only racemized material would result, a satisfactory alkaline hydrolysis process was evolved and a high purity non-racemized glutamate made commercially available.

Commercial manufacture of the sodium salt of glutamic acid, monosodium glutamate, which will generally be referred to in this paper by the accepted abbreviation "glutamate," is not, like so many of our present day pure chemical substances, dependent on synthetic processes but rather on the separation of glutamic acid from natural proteins, usually of vegetable origin.

Glutamic acid was first isolated from proteins in 1866 by the German chemist Ritthausen, who introduced into protein chemistry the experimental method of acid hydrolysis and the subsequent precipitation of barium or calcium salts of certain of the amino acids by means of an alcohol.

Chance played a part in Ritthausen's isolation of glutamic acid for one of the proteins he worked with was gliadin, a component of wheat gluten which includes in its structure approximately 40% glutamic acid. Ritthausen observed that his gliadin hydrolysate contained an acid strong enough to decompose calcium carbonate, and that after concentration of the hydrolysate and separation of tyrosine, the acid substance could be obtained by fractional crystallization.

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Although forgotten for many years, Ritthausen's work formed the twentieth century basis for the first practical glutamate manufacturing operations.

Glutamic acid was successfully synthesized by Wolff in 1890, his starting material being levulinic acid and, in the intervening years, many other syntheses, using other starting materials, have been devised. Compared to the technology of production from proteins the presently known synthetic methods are much more costly. The successive steps in all published syntheses are involved, intermediate yields are low and the product obtained is usually the racemized inactive form which is difficult to convert to the active or dextro configuration.

While it can be said that the interesting flavor building properties of glutamate were not recognized until recent years, this is true only when reference is confined to intentionally prepared monosodium glutamate. It seems a reasonably safe assumption that the contribution of a glutamate to the building up of food flavors stems back to the discovery of the processes used in the Orient to convert soya beans into soya sauce. The slow conversion of the soya bean meal portion of the basic materials used for soya sauce preparation is in part due to the action of vegetable enzymes and the resulting splitting off of various amino acids, particularly glutamic, soya bean meal containing approximately 20% of glutamic acid. Enzymatic hydrolysis usually results in formation of ammonia from acid amides, and Oriental soya sauce has been found to contain ammonium complexes of amino acids, including ammonium glutamate. Ammonium glutamate undoubtedly plays a part in building up the flavors associated with soya sauce, and it is of some interest that from the time monosodium glutamate became commercially available it has been customary in the Orient to use it as a flavor reinforcement in soya sauces.

Whenever the history of monosodium glutamate as a flavor builder is reviewed, speculation arises as to why, for more than forty years, the many workers in the field of protein chemistry isolated glutamic acid, prepared its salts, and studied the chemistry of those interesting compounds in detail, without ever exploring other than their purely chemical aspects. As an example, wheat gluten hydrolysates, after neutralization with sodium hydrate or carbonate and conversion of the excess hydrochloric acid to common salt, have somewhat appetizing odor and flavor suggestive of condimentary value, yet from 1866 to sometime after 1900 there is no evidence of the discovery of the flavor-building properties of the sodium salt of glutamic acid, which is necessarily an important component of such hydrolysates.

Recognition of the advantage of a salt-like seasoning material in the form of a definite chemical compound over the then available soya

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sauces of highly variable flavors, has to be accorded to Kikunae Ikeda of Tokyo, Japan. In a brief paper contributed to the Eighth International congress of Applied Chemistry, held in New York in 1912, Dr. Ikeda expressed an interest in the use of a dried seaweed, LAMINARIA JAPONICA, in Japanese cookery, and stated that he had undertaken determination of the substances to which it owed its flavoring properties. Hydrolysis of the seaweed resulted in partial separation of glutamic acid from other amino acids and the discovery that when neutralized with soda, the sodium glutamate (inevitably in impure form) exhibited a desirable meat-like taste.

As to the flavor characteristics of sodium glutamate the first printed reference known to the writer appears in British Patent No. 9440, issued April 21, 1909, to Kikunae Ikeda, on an application filed the preceding year, the title of the patent being "Manufacture of Flavouring Material."

The process, which did not prove commercially practical, was based on the electrolysis of an albuminous hydrolysate, from which excess acid had been removed, under conditions which would result in accumulation of the sodium salt of glutamic acid in the anode compartment of the diaphragm cell.

Saburosuke Suzuki and Company of Tokyo became interested in Ikeda's experimental work and, as the outcome of an arrangement apparently made in 1910, studies of processes were carried on by the Suzuki Co. under Ikeda's general direction, with continuance of research in Ikeda's own laboratory in the Imperial University of Tokyo. Suzuki and Company, either directly or as assignees of Ikeda, obtained a number of patents in most world countries on glutamate processes. The manufacture of glutamate, sold under the trademark AJI-NO-MOTO, not only became the principal Suzuki product, but the substantial output placed the Suzuki company in a dominant position in the glutamate industry.

The basic Suzuki-Ikeda patents expired in 1929 and seven years later, according to a 1936 report of the U.S. Trade Commissioner in Japan, there were some seventy small concerns manufacturing glutamate in Japan by hydrolytic processes from wheat gluten, Suzuki and Company accounting for more than half the total Japanese output. In the mid-1930's Suzuki and Company used extracted soya bean meal as their primary raw material, apparently for the dual reasons that (1) the protein separated from Manchurian soya meal was a cheaper source of glutamic acid than gluten separated from wheat and (2) that the large tonnages of wheat starch left after gluten removal presented a difficult marketing problem in the Orient, which the de-proteinized soya meal, readily salable as a low grade fertilizer, did not.

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AJI-NO-MOTO and the brands of the minor Japanese producers were made in surprisingly large amounts, data in the writer's possession indicating the annual output of all Japanese manufacturers to have reached 10,000,000 pounds in 1933. The actual production of glutamate may have been 10% to 15% less as most of the smaller producers, but not Suzuki and Company, sold products extended by anywhere from a few percent up to thirty percent of common salt.

Japanese exports of "seasoning materials," principally glutamate, totalled 2,268,000 pounds in 1934, the major portion going to Asiatic countries.

The growth of glutamate production from zero to approximately 9,000,000 pounds in the first twenty years of its manufacture in Japan perhaps calls for comment, as the growth rate and output exceed the corresponding figures for United States production in the past twenty years.

Oriental diets are greatly restricted as compared to those available to all levels of the population of this country, as well as to a majority of European peoples prior to the war. The monotony of taste of the foodstuffs available to the majority of Orientals was probably responsible for the development of soya sauce, and for the addition of small amounts of glutamate to soups, rice and fish dishes, and to soya sauce itself. But these small amounts represent a large total tonnage.

In 1921 the manufacture of glutamate was undertaken in China, the processes adopted being necessarily simple and direct. Expensive equipment could not be provided and although hydrochloric acid was made on a small scale by one concern in Shanghai, principal supplies had to come from Japan, so recovery of hydrochloric acid from the hydrolysate was essential. Chinese wheat contains much less protein than American, so wheat flour had to be imported from Canada, the starch disposal problem not being difficult in view of the limited production. It was estimated that Chinese production was of the order of 350,000 pounds in 1930. A few years later the Chinese material was beginning to compete with the Japanese product in Singapore, Malaya and the Philippines.

Manufacture was carried on in several plants in China, principal production centering in the Tien Chu factory, managed by Poo-Nien Wu, who was responsible for the development of an alcohol purification step which made his company's "VE-TSIN" almost competitively equal to Suzuki'a AJI-NO-MOTO. Wu's process is described in British Patent 258,655 of September 24, 1926.

When the Japanese invaded the coastal provinces of China in 1937, the Chinese glutamate plants were promptly and totally put out of commission and, although Japan evacuated all its troops from China

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in 1945, the unbalanced state of the Chinese economy has not yet permitted an effective rebuilding of the industry.

Meanwhile the partly successful attempts of Suzuki and Company to introduce AJI-NO-MOTO into the United States had created some interest in glutamate processes in this country, adoption of glutamate as a flavor-building agent in a few types of prepared soups indicating the possibility of developing demand for a domestic product. Suzuki's efforts to put AJI-NO-MOTO on dinner tables and in home kitchens in this country did not meet with much success, the apparent reason being a lack of understanding of essential differences in merchandising procedures of the Orient and those of the United States.

Credit for the first attempt to produce glutamate in this country belongs to the Huron Milling Company of Harbor Beach, Michigan. Manufacturing a variety of special starches, including wheat, this company had a wheat gluten by-product, a logical starting material for glutamate production. Very little has been published about the early days of the venture or the difficulties which had to be surmounted before an acceptable product, equal to the Suzuki material, was produced. The writer regrets his inability to fill in this part of the history of glutamate in the United States, but hopes the appearance of his paper will result in the subsequent publication of Huron Milling Company's story of their efforts and ultimate success.[1]

By 1926 wheat gluten had become the standard raw material for glutamate manufacture in the Orient and for the first American venture into its production. Hydrochloric acid was the preferred hydrolytic agent so, basically, the materials for commercial production were those used by Ritthausen in his laboratory sixty years earlier, when he made the first separation of glutamic acid from a protein. Each of the manufacturers evolved some special technics and processing steps, and as yields were the prime measure of costs, the individual factory methods of separating and purifying glutamic acid and converting it into monosodium glutamate of acceptable crystal form, free from dusty particles, were jealously guarded secrets which were not made the subject of patent applications.

Raw materials other than wheat gluten were of course made the basis of experiments, and patents were obtained by nationals of many countries on the processing of practically every available protein known to contain recoverable amounts of glutamic acid.

Turning now to the story of a prolonged but ultimately successful attack on the problem of using other starting materials than wheat gluten, the writer can substitute first hand knowledge for the frag-

[1]An account of the Huron Milling Company's contribution was supplied subsequent to the Symposium by Mr. Galvin and is included at the end of this paper under Addendum.

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associates, undertook the packaging and merchandising of an anti-freeze in competition with alcohol and glycerine. For a few weeks all was well, then irate customers with plugged up or leaking radiators began to claim damages, the engineer went out of business, and Larrowe once again had Steffens waste concentrate on his hands.

To discover what had created the anti-freeze difficulties Larrowe had some of the concentrate analyzed. The list of what was in it was impressive so sometime later Larrowe made arrangements for a complete investigation and an evaluation of its potentialities as a raw material for a chemical process.

These possibilities seemed to center in potash, betaine and amino acids and, after some institutional laboratory work a process was sketched out, the classical use of hydrochloric acid for the hydrolysis step being one of its features.

Without going through a pilot plant stage, Larrowe began construction, on the basis of little more than laboratory data, a commercial unit adjacent to his feed mill in Rossford, Ohio. A chemical journal reference to the plant construction and its expected output of glutamate was brought to the attention of S. Suzuki and Company by their New York representative, and Larrowe received a cable from S. Suzuki and Company, advising that Chuji Suzuki, their managing director, was en route from Tokyo to Rossford to discuss a sole agency or other form of sales agreement.

Believing sales development of glutamate in the United States would be a slow and costly matter, whereas Suzuki and Company could readily dispose of the Rossford output in the Orient, Larrowe expressed willingness to make an agreement but only on condition that Suzuki and Company become a partner in the manufacturing enterprise and contribute 40% of the capital.

Reading through the Larrowe-Suzuki Company agreement of May 20, 1926, as a memory refresher, the writer is of the opinion Bret Harte could have effectively substituted a member of another Oriental race in the last line of one of his poems, for the agreement not only recites the fixed prices to be paid by Suzuki and Company but includes the further provision that Larrowe could not sell glutamate for "use in human food" except to Suzuki and Company. Incidentally, the schedule of prices represented no more than bare costs and it may not be unfair to surmise that glutamate manufacturing costs were well known to Mr. Chuji Suzuki, but not to James E. Larrowe.

Basically the process to be used at Rossford involved the removal of betaine hydrochloride and potassium chloride by saturation of hot Steffens concentrate with gaseous hydrochloric acid, followed by hydrolysis after further addition of hydrochloric acid.

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mentary information furnished him by the Oriental producers on which the previous part of this paper has had to be based.

Before discussing this particular operation it seems desirable to introduce, by way of preface, an interesting personality, the late James E. Larrowe, for it was his outstanding quality of seeing things through that resulted, after ten years of effort, in the first effective use of a new raw material and an alkaline hydrolysis process.

James E. Larrowe was a beet sugar entrepreneur, engaged through sixty of the eighty years of his life in building and operating beet sugar mills. He installed beet pulp driers in mills at his own expense and utilizing the dried pulp as a by-product, he created an extensive livestock feed business. His primary interest, of course, was the profitable disposal of the dried beet pulp.

His Larrowe Construction Company, between 1910 and 1919, built ten beet sugar mills with a total daily slicing capacity of 9,000 tons of beets, and by 1919 he had beet pulp flowing into his feed mills and his selling agency from some fifty mills.

The trademark LARRO was a familiar embellishment of country feed stores many years before Mr. Larrowe sold out to General Mills in 1929 and re-entered beet sugar manufacture.

During World War I the United States was desperately short of potash, for 90% of the fertilizer industry's supplies had been imported from Germany. No effort was made to control prices of domestic potash, for high prices were incentives to production from every possible source and, at $400 per ton for fertilizer grade muriate, there were not many overlooked, including the Steffens waste water from beet sugar mills. In 1917 five, and in 1918 eight, beet sugar mills were processing Steffens waste for potash, Larrowe's Mason City, Iowa, mill among them.

Potash recovery from these dilute waste waters included concentration to almost a molasses consistency as a preliminary to burning off the carbohydrates and collecting the potash ash. The concentrated waste water was stored in steel tanks, and when the Armistice was declared Nov. 11, 1918, Larrowe had several thousand tons in his Mason City tanks, and a sudden end to his potash business. The concentrate was now of little value, so it was left in the tanks in the hope that some profitable use could be found for it. The hard winter of 1920, when temperatures fell to 30 below zero at Mason City, provided the next happening, for one of the engineers noticed a small leak at a tank seam and that despite the low temperature the concentrate was not losing its flowing properties. Here, obviously, was a new anti-freeze for automobiles, so the engineer made a deal with Larrowe and, with some

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Chemical plant equipment had not then been developed to a reasonable degree of resistance to hot concentrated hydrochloric acid so, in retrospect, it is not too surprising that after 33 days of operation, early in 1927, severe corrosion of pumps, pipe lines, etc., made it necessary to shut the plant down and study what could be done to improve the chances of success.

Apprised of the equipment problem by Mr. Larrowe, his copartner, Suzuki and Company, suggested trial of a different hydrochloric acid process, involving lower concentrations and temperatures, which had been devised by Dr. Ikeda and patented prior to inception of the Rossford project. After installation of some new equipment the plant was started up again, but at the end of three months corrosion difficulties once more caused a shutdown.

At this point the writer was called in as a consultant and asked for an opinion on the practicability of a hydrochloric acid process. It seemed obvious that failure of equipment more than failure of the process was responsible for the difficulties, and the recommendation was made that no further trials be undertaken until either satisfactory equipment could be obtained, which was doubtful, or some other hydrolysis agent substituted for hydrochloric acid.

The report was forwarded to Suzuki and Company and in November 1927 Dr. Ikeda and Mr. Chuji Suzuki arrived at Rossford with a new process Dr. Ikeda had rather hurriedly worked out following the failure of the first hydrochloric acid process.

This new process substituted sulphuric for hydrochloric acid and included the step of precipitating glutamic acid as calcium glutamate. By this time Mr. Larrowe, wary of plant scale experiments, agreed with the writer that the limit was a pilot plant of a few hundred gallons capacity assembled from available apparatus. The pilot plant was put into operation December 1927 and ran spasmodically, with many changes, through 1928.

Approximately 70,000 pounds of glutamic acid, which did not fully meet the specifications in the Larrowe-Suzuki agreement, were produced in the year 1928. Costs were quite unattractive, so the third process, which never got beyond the pilot plant stage, was abandoned.

In March 1929 Dr. Ikeda returned to Rossford with a modification of his sulphuric acid hydrolysis process, and again its study was confined to pilot plant trials. The supposed improvements did not materialize, and for the next six months purification of the stock of crude glutamic acid was intensively studied in the Rossford laboratory and a small scale commercial unit, which included a monosodium glutamate section, was built.

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Despite four fruitless attempts to produce glutamate, and expenditures which had run into several hundred thousand dollars of "my own chips," as Mr. Larrowe said—for Suzuki and Company, while making promises, had not provided much more than its original contribution—Mr. Larrowe was not yet willing to accept the advice of his beet sugar associates and to give up the Rossford project.

The writer had followed, still as a consultant, the unsuccessful attempts to hydrolyze Steffens concentrate with acid, and when asked whether there was any chance of ever devising a profitable extraction procedure he told Mr. Larrowe there was a 50-50 chance, but that the chance centered on the discovery, through research, of some new means of unlocking glutamic acid from its stubborn associates in the raw material.

Mr. Larrowe's decision was typical of many of those he had made in earlier years, for he promptly said, if the writer would, at his own expense, supervise research at Rossford, undertake whatever other research might be necessary elsewhere and put up half the cost of the inevitable pilot plant, he would take care of Rossford research costs and, if anything promising resulted, he would equip the plant to meet the new needs.

Out at Mason City, Iowa, most of the Steffens concentrate was still in the tanks, for the withdrawals had been only a few hundred tons; thus there was assured for processing a supply of raw material equal to at least half a million pounds of glutamic acid—if a process could be devised. It seemed a worthwhile gamble of some time and some money, and an arrangement was made and serious research started.

From the beginnings of the Rossford project everyone, including Dr. Ikeda, had believed the statement in textbooks on amino acids that:

"When a protein is hydrolized by an alkali, its constituents, with the exception of glycine, are racemized."

and:

"Glutamic acid is particularly sensitive to hot alkalies, racemization to the inactive form being inevitable."

With no inhibitions, as a result of several years of observations of acid processes which did not live up to published statements, it seemed desirable to check up on the alleged racemization. Experiments carried out under the same temperature conditions as acid hydrolysis did give a racemized product, but it was not completely racemized, so the "inevitable" was crossed out and an approach to a possible solution undertaken by a very lengthy series of experiments in which small variations in alkali concentration, temperature and time were separately studied.

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It was found that there was no racemization at appropriate relations of all three factors, and a new process was on the way to being born. Patent applications were filed in all countries where a beet sugar industry existed, and it was not in the least surprising that the German Patent Office insisted on experimental proof that the process resulted in anything other than racemized inactive glutamic acid, in view of citations the Patent Office quoted from eight published works. The demonstration was made and the patent granted—in 1940 on an application filed in 1932.

The pilot plant was built at Mr. Larrowe's expense for, with a workable method in sight, the sharing of cost had lost its point. For the next five years, or until 1936, the pilot plant was gradually enlarged, new sources of Steffens concentrate were developed, and then the original Rossford plant was rebuilt to suit a process which had no corrosion problems and gave satisfactory yields. The rebuilding followed the ending of the Larrowe-Suzuki partnership, an interesting story in itself but too long for inclusion in this paper.

In the Amino Products Company, as the rebuilt plant was named, I became vice-president and a small stockholder and had the pleasure of following the growth of the enterprise through to the end of 1942 when, owing to Mr. Larrowe's ill health, and the writer's preoccupation with problems in another unrelated plant, it seemed desirable to turn it over to some concern able and willing to build a second alkaline hydrolysis plant on the Pacific Coast, the beet sugar industry of the Middle West being by that time unable to supply the needs of the Rossford unit.

Sale of Amino Products Company to International Minerals and Chemical Company was concluded in December 1942. The plant on the Pacific Coast has been built, and after some tribulations which rather closely resemble those associated with the early Rossford difficulties with alkaline hydrolysis, International's San Jose glutamate plant is now producing at, or slightly better than, its designed capacity.

James E. Larrowe died, at the age of eighty, in December 1943. If it should seem that the outline of his long but ultimately successful efforts to produce glutamate from Steffen's concentrate has been overly lengthy in the telling, the writer's excuse is that the story is known only to Mr. Larrowe's friends, and that he has taken the opportunity afforded him to give public recognition to the tenacious and unconquerable spirit of a former associate. Of him it can be said, in the words of Shakespeare:

"For what I will, I will, and there an end."

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Addendum

Brief History of Huron Milling Company Monosodium Glutamate Operations

The entry of the Huron Milling Company into monosodium glutamate manufacture was largely influenced by the fact that it had been producing wheat gluten along with wheat starch as far back as 1900. Wheat gluten is an excellent source of glutamic acid and when an outlet for wheat starch is available it can be a most economical raw material for glutamate manufacture. The Huron Milling Company became interested in glutamate when Oriental imports began to be considerable.

Consequently in January, 1929, experimental work was initiated in the laboratories under the supervision of Mr. A. J. Patten, the Director of Research. Amino acid technology was very familiar to Mr. Patten, who had spent a number of years working with Kossel, a pioneer in amino acid chemistry at Heidelberg. It was obvious that the manufacture of monosodium glutamate required a great many processes for which large-scale production equipment was not then available. All possible procedures were studied with the view of selecting the one which showed the most promise of being successful in large-scale production. This work led to the conclusion that hydrolysis of gluten with hydrochloric acid, isolation of the glutamic acid as its hydrochloride, with subsequent crystallizations as free glutamic acid and monosodium glutamate would be the best procedure.

With the cooperation of members of the production and engineering staff, equipment was designed and installed early in 1934. The first commercial production was made in August of that year. Since that time a great many modifications and improvements in both process and equipment design have been made. Particularly, improvements have been made in fabrication of equipment from hydrochloric acid-resistant materials such as plastics, ceramics, alloys and other materials. Undoubtedly the company has contributed its share to the nation's fabricating techniques for building this type of equipment.

The Harbor Beach factory produces a very large tonnage of high purity glutamate in orderly round-the-clock operation.

Discussion

Dr. Dove: I would like to raise the question as to the work that Dr. Tressler did on glutamate production.

Mr. Bishop: I think Dr. Tressler comes in, in connection with the Mellon Institute. Although the author does not mention the Mellon Institute, that is where Larrowe placed the problem prior to the Suzuki partnership. From that initial contact he got the process which later led to the joint efforts with the Japanese.

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Quality Production of Glutamate

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Author's abstract

Monosodium glutamate is manufactured at the present time by three companies with a fourth soon to begin operations. In general, many of the production problems are similar regardless of the particular operation. The process used in one plant is described in considerable detail with slides showing equipment used and special processing operations.

Processing steps are essentially (1) hydrolysis to free the glutamic acid from other substances, (2) separation of the glutamic acid, (3) purification of the glutamic acid, (4) conversion to monosodium glutamate and (5) crystallization, separation and drying of the purified monosodium glutamate.

Glutamic acid occurs in three forms, the active (natural) L-form, the inactive D-form and the racemic mixture of the two modifications. Only the active form occurs naturally and is the form made commercially. It is the monosodium salt of this form which has the unique power of flavor enhancement when added to foods.

In the processing plant described in this paper Steffens filtrate, the desugared molasses from beet sugar plants, is hydrolyzed with alkali then acidified with hydrochloric acid and concentrated. After removal of mineral salts the filtrate is adjusted carefully to the isoelectric point of glutamic acid which crystallizes out over a period of 5 to 6 days. This glutamic acid is then refined, neutralized with caustic soda solution and monosodium glutamate crystallized from this neutral solution. Quality control is the keynote throughout the operations.

Monosodium glutamate can be made in three modifications. In accordance with the currently accepted nomenclature these are designated as the L-, the D- and the DL-forms, the last being an equal or racemic mixture of the first two. The L-form is the naturally occurring isomer and is the only form that has the power of intensifying the flavors of foods; it is the one which is of interest to food technologists. The D-form appears to be of no aid whatever in flavor enhancement.

Glutamic acid is one of the most common of the amino acids and is a constituent of practically all proteins. The quantity however varies in the different proteins. Certain other non-proteins also contain glutamic acid or precursors of glutamic acid. Liberation of the acid from its natural sources invariably begins with an hydrolysis. This can be effected in three general ways, through the use of enzymes and by heating in the presence of an acid or an alkali as the hydrolyzing agent. In the present day production of glutamic acid, the latter two methods are the ones used.

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Hydrolysis of a protein in an alkaline solution liberates the glutamic acid in the racemic or DL-form and no method has so far been developed for the prevention of this racemization. However, alkaline hydrolysis is used satisfactorily in the commercial manufacture of monosodium glutamate from beet sugar solutions in a process which is the subject of this paper.

Glutamic acid can be made in a number of different ways by organic synthesis (52). Such synthesis has always resulted in the racemized mixture. So far, no method has been devised for resolving the racemic mixture at a cost low enough to allow this method to compete with production by hydrolysis of natural raw materials from agricultural sources (22, 78).

Since glutamic acid is only one of the many complex organic chemical substances present in such raw materials, its separation and purification is a complex process with many steps (Fig. 1) and therefore a high recovery presents many difficulties. The limitation has restricted the basic raw materials for commercial production in the United States to three sources. These are wheat gluten (38), corn gluten (7, 76) and the sugar beet (53, 54, 70). A fourth raw material, soy bean protein, is used in the Orient (12).

Production of food-grade monosodium glutamate in this country is at present carried out in four factories operated by three corporations. These are the Huron Milling Company at Harbor Beach, Michigan, using wheat gluten; General Mills, Inc., also operating on wheat gluten; and International Minerals and Chemical Corporation, with plants at Rossford, Ohio and San Jose, California. The Rossford plant originally operated on beet sugar solutions, but was later converted to utilize wheat and corn glutens. The San Jose plant uses beet sugar solutions only.

Another major producer, the Staley Manufacturing Company, is expected to begin operations at Decatur, Illinois, this spring. It is understood that corn gluten is to be used as a raw material at the Decatur plant.

As the glutamic acid concentration decreases in any raw material, satisfactory commercial operation depends more and more upon constant markets for by-products at good prices.

Glutamic acid exists in the sugar beet in the form of glutamine. This quite largely passes into the raw juice without decomposition during the diffusion step in the process. The organic nitrogen in the sugar beet is the source of some trouble to the manufacturer of beet sugar, and for many years the beet sugar industry has endeavored to breed strains of beets that are high in sugar and very low in what they term "harmful nitrogen." These efforts have been successful and sugar beets usually vary from .05 to .12% glutamic acid. In general the

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SIMPLIFIED FLOW SHEET

Monosodium Glutamate from Steffens Filtrate by the I.M.& C.C. Process

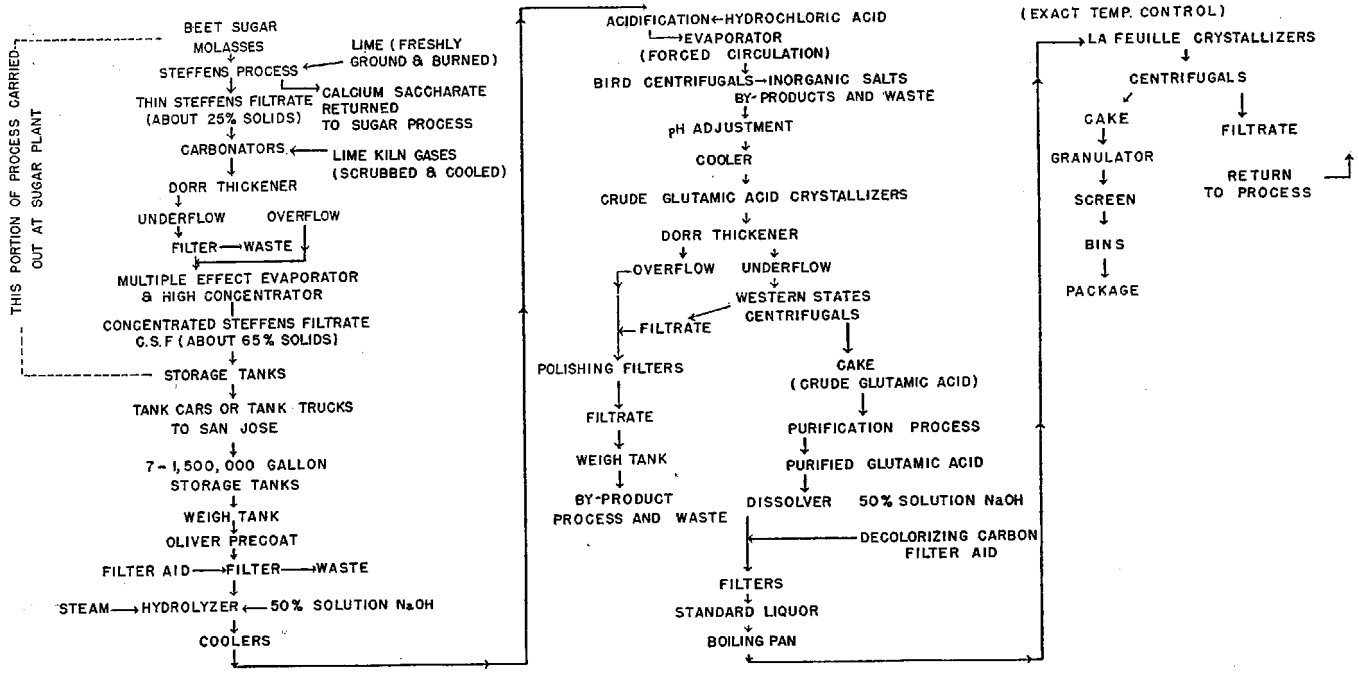

Fig. 1—Siplified flow sheet showing steps in the manufacture of monosodium glutamate.

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glutamic acid content of beets grown in the Snake River Valley (Idaho) and on the eastern slope of the Rocky Mountains is lower than of those grown in California and in the Midwestern States. The use of nitrogen in any form as a fertilizer increases the percentage of glutamic acid in sugar beets, but it also lowers the percent of sugar although it may increase the amount of sugar produced per acre because of increased tonnage of beets produced.

When the diffusion juice begins on its trip through the sugar plant, it is first made alkaline with lime. During this process much of the glutamine changes to pyrrolidone carboxylic acid which is the internal anhydride of glutamic acid. Equilibrium is such that in any aqueous solution of either glutamic acid or pyrrolidone carboxylic acid both are present. As the solutions move on through the sugar plant the final products, of course, are sugar and molasses, and under the conditions of the process most of the glutamic acid is present in the molasses as pyrrolidone carboxylic acid.

Molasses is normally desugared by what is known as the Steffens process. In this process the molasses is diluted with water to about 5 or 6% sugar and is then treated with freshly burned and freshly ground lime. The calcium oxide combines with sugar to form calcium saccharate which is relatively insoluble and is removed by filtration and returned to the sugar process. The filtrate from the filter press is commercially known as Steffens waste water and contains approximately 2½% solids. If the dilute waste water is allowed to stand at ordinary temperatures it is subject to bacterial spoilage, but when concentrated to 60 or 70% solids it keeps indefinitely without difficulty.

In the production of glutamic acid from this source, the Steffens filtrate is first carbonated with lime kiln gases. The calcium carbonate thus formed is removed by settling and filtration, and the clarified weak filtrate is then concentrated in large multiple effect evaporators. This

Fig. 2—Oliver precoat filter used to filter the concentrated Steffens filtrate as it enters the plant for processing.

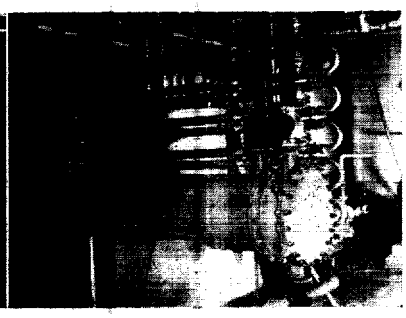

Fig. 3—Karbate heat exchanger for preheating filtrate on its way to evaporator.

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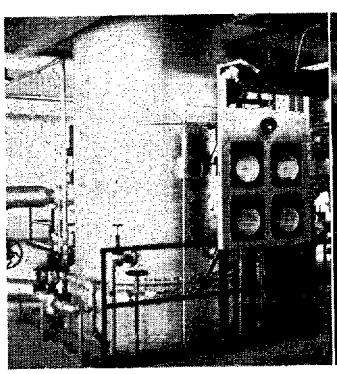

Fig. 4—Single effect calandria evaporator for concentration of filtrate.

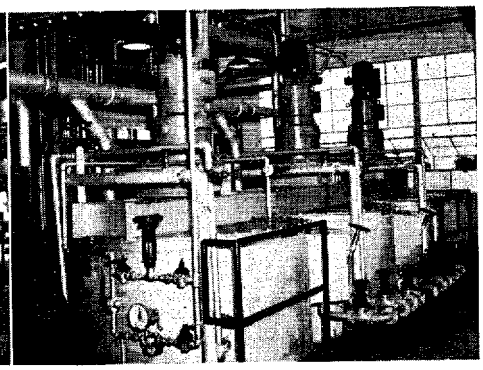

Fig. 5—Hydrolyzers in which the filtrate is hydrolyzed with caustic soda solution.

entire process is continuous and is carried out as the thin filtrate is produced. The concentrate is then shipped to San Jose by tank truck or tank car and stored in seven large tanks, each of 1,500,000 gallons capacity. In use the raw material is drawn from the storage tank, weighed and then filtered through a filter aid by means of an Oliver precoat filter (Fig. 2). This removes any suspended solids. The concentrated Steffens filtrate, now termed C.S.F., is passed through a heat exchanger (Fig. 3) and is brought to a uniform density by a primary evaporator (Fig. 4). Following this the concentrate is hydrolyzed in steel hydrolyzers with a 50% solution of caustic soda (Fig. 5). The hydrolyzed liquor is then passed through coolers and is acidified with

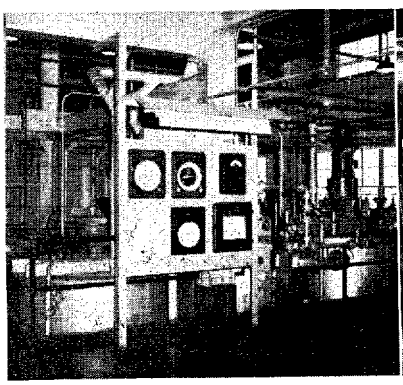

Fig. 6—Neutralization station showing instrument control panel for exact control of pH.

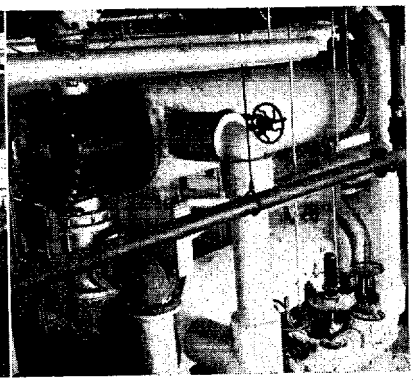

Fig. 7—Neutral solution is preheated in these Karbate heat exchangers before going to evaporator and inorganic salt removal station.

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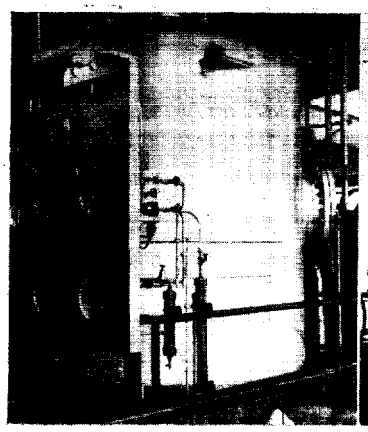

Fig 8—Evaporator for concentration of the acidified filtrate.

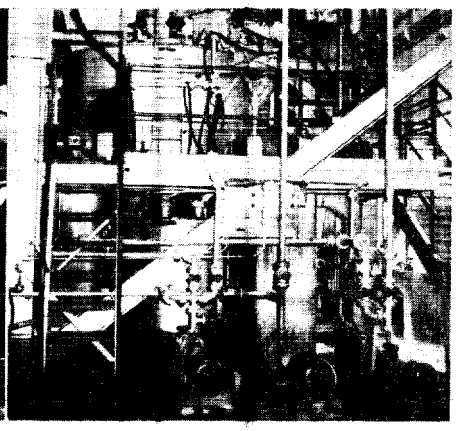

Fig. 9—Bird continuous centrifuge station for removal of mineral salts before further acidification and crystallization of glutamic acid.

hydrochloric acid (Fig. 6). The acidified liquid is then concentrated at high vacuum in an evaporating system consisting of an outside heater (Fig. 7) and a rubber-lined flash chamber (Fig. 8). Originally a carbate heater was used, but it proved unsatisfactory and was later replaced with one made from a special type of stainless steel.

During the concentration some inorganic salts such as potassium chloride and sodium chloride are precipitated; these are removed by being passing through Bird centrifugal filters (Fig. 9).

Following this, a final pH adjustment is made (Fig. 10) and the highly acid liquor is then passed through coolers refrigerated by means

Fig. 10—Acidification station where HCl is added to form glutamic acid.

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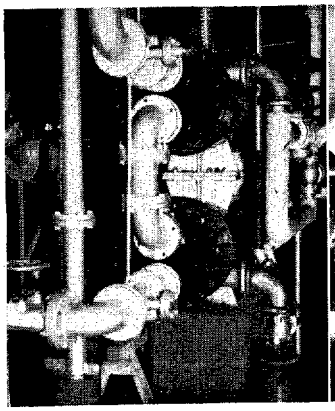

Fig. 11—Refrigerated Karbate heat exchangers for cooling acidified solution.

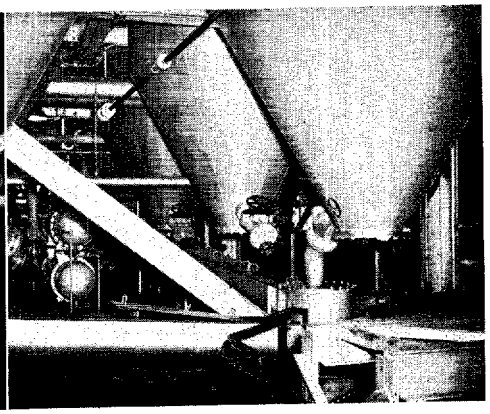

Fig. 12—Glutamic acid crystalizers.

of a vacuum refrigerator system (Fig. 11). The filtrate is then run into large rubber-lined crystallizers, there being twenty of these (Fig. 12). At the end of five days the crystals of glutamic acid along with additional crystals of sodium chloride have been formed and the slurry is passed into a rubber-lined Dorr thickener. The solid material in the underflow from the Dorr thickener is removed by Western States sugar-type centrifugals. The filtrate joins the overflow from the Dorr thickeners and passes through polishing filter presses (Fig. 13). Filtrate from these presses is then weighed and passes to by-products operations or to waste. The cake from the filter presses and centrifuges, which contains glutamic acid, sodium chloride and some organic substances, is now passed through the purification process.

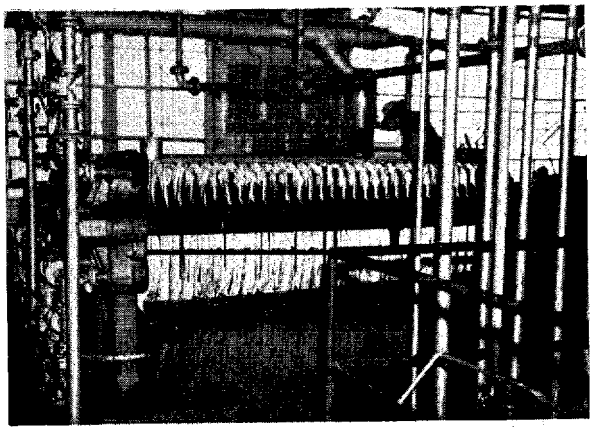

Fig. 13—Plate and frame filter press for filtering off last traces of glutamic acid crystals after centrifugalization.

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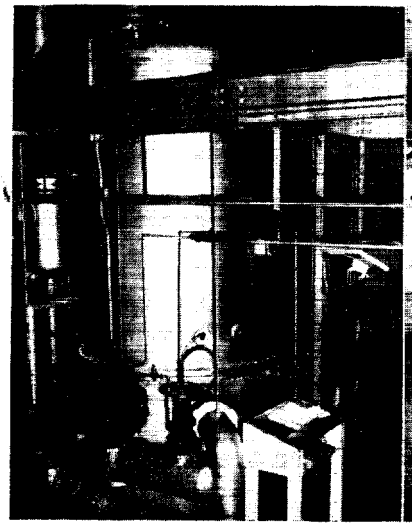

Fig. 14—Single effect evaporator for concentration of the monosodium glutamate solution prior to crystallization.

Fig. 15—Drum drier and hummer screen for final drying and screening of monosodium glutamate crystals.

From this point on, all parts of the process are carried out in stainless steel equipment.

Glutamic acid crystals so produced are then dissolved in a caustic soda solution and the resulting liquid decolorized with activated carbon and finally concentrated in a stainless steel, calandria type, single effect boiling pan (Fig. 14). The monosodium glutamate is crystallized in the La Feuille type crystallizers. These crystallizers are automatically controlled, being cooled with water from the refrigerating system. The crystals are separated by means of a centrifuge and then dried in a rotary dryer or granulator (Fig. 15). The product is now placed in 200-pound drums and after testing is ready for shipment.

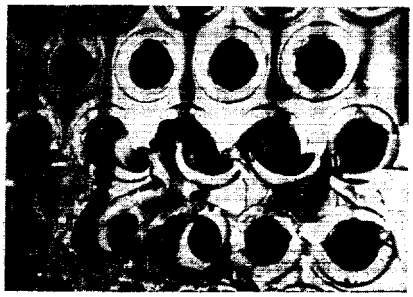

Fig. 16—Dismantled heat exchanger showing severe corrosion which has taken place.

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The manufacture of monosodium glutamate by any process at present in use is not easy. Raw materials are not uniform in quality or composition. Moreover, the raw material supply is not constant and in the case of the cereal proteins, fluctuates widely in cost. Acid treatment of glutens produces a large number of different substances besides glutamic acid, and the difficulties encountered in removing the glutamic acid from such mixtures are evidenced by losses in the process. In the case of Steffens filtrate, similar complicating materials are produced in both the beet sugar operations and the subsequent process by which the glutamic acid is recovered.

These, with corrosion difficulties and those met with in the development of by-products, are still problems of major importance in this industry.

References: (7) (12) (22) (38) (52) (53) (54) (70) (76) (78)

Discussion

Mr. Galvin: You mention stainless steel as being resistant. I wonder if you have used anything more resistant than 18-8 M.O.

Dr. Manning: The type we have found most satisfactory is type 316, which contains molybdenum; I believe this is the same as 18-8 M.O.

Dr. Anson: Why isn't it feasible to extract the pyrrolidone carboxylic acid with an organic solvent?

Dr. Manning: We have thought this to be feasible, but so far we have not been able to carry out the extraction on concentrated Steffens filtrate. This is apparently due to the effect of other materials present.

Dr. Melnick: Don't you have a very poor partition coefficient?

Dr. Manning: The coefficient is quite low using aqueous solutions of pure pyrrolidone carboxylic acid, but that difficulty would not make a process impossible. So far, our research department has not been able to work out a process based on extraction by organic solvent due to the difficulty mentioned.

Dr. Fellers: Do you get any racemization at all by your method? Don't you get some of the inactive form in the product?

Dr. Manning: Under certain conditions, it is possible to have quite a lot of racemization. The effect of bacteria and certain other agents may cause racemization. We did have some trouble at the start, but we have been able to overcome this difficulty and to keep the inactive form practically down to zero.

Dr. Melnick: Would you care to mention what laboratory control procedures are used in your operation?

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In all methods for the manufacture of monosodium glutamate corrosion problems are of great magnitude. Not all of them have been satisfactorily solved. For instance, some difficulty has been encountered in securing rubber-covered equipment which is mechanically satisfactory. This was especially true when government regulations required a certain percentage of synthetic rubber be mixed with natural rubber.

Some types of stainless steel have been found to be satisfactory although not in the presence of hydrochloric acid. Where corrosive solutions contain suspended crystals of glutamic acid or salt, erosion is also a factor (Figs. 16 and 17).

Production at the San Jose plant now exceeds 9,000 pounds of monosodium glutamate per day.

In the design of the plant considerable study was given to designing the equipment so that no unpleasant odors or fumes would be given off at any point in the process. In handling raw materials of this type, and the reagents used in the process, it is possible for somewhat noxious fumes to be evolved. These include oxides of nitrogen, acid vapors, etc. All of the tanks are covered and vented through a scrubbing system which removes any gases of an acidic character. The scrubbers are finally vented through the boiler stack. This greatly improves the working conditions, and in addition, is beneficial to the appearance of the plant.

Several processes using ion exchange resins for the separation of glutamic acid from hydrolysates have been proposed and are being tried out experimentally. Ion exchangers are also being tried out in the beet sugar industry. The technology and economies of all of these applications have not yet been entirely determined.

Fig. 17—Pump rotor corroded beyond further use.

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Dr. Manning: The operations used at the San Jose plant are carried out for control of purity and control of economies of the process. Complete laboratory control is used at each step in the process. This includes the determination of glutamic acid by both the pyrrolidone carboxylic acid method and the polariscope. Dr. Blish and Dr. Hac have been working on two other methods for determination of glutamic acid—the microbiological method and a new method—the decarboxylase method. The latter uses an enzyme and appears to have great promise. It is not yet being used in the plant.

Mr. Nair: In the final separation of centrifugation, is it necessary to have any rubber lining on the equipment?

Dr. Manning: We have type 316 stainless steel baskets. We did use rubber lining at first, but it was not satisfactory.

Dr. Anson: In other great beet producing regions of the world, what is the glutamate content of the waste?

Dr. Manning: As far as I know, there are no beet sugar plants anywhere else in the world which produce Steffens waste. I do not believe there ever was a Steffens plant in Germany, although the process was developed there. In this country the Steffens waste is most lean in glutamic acid in the Rocky Mountain area; the material produced in Iowa and the Midwest is fairly high in glutamic acid.

Meat Flavor and Observations on the Taste of Glutamate and Other Amino Acids

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Author's abstract

A direct study has been made, using a taste panel, to determine the truth or falsity of the impression that monosodium glutamate has a meaty or "chickeny" taste.

Meat was investigated to arrive at the characteristics of "meaty" flavor, starting with unaged, lean beef, and including pork, lamb and chicken in the investigation. The beef was divided into juice and fiber and each of these was examined separately for flavor, in the cold state and after moderate heating. It was found that the characteristic meaty flavor which is developed on heating is derived from meat fiber rather than from juice, that it consists almost entirely of odor, and that chemically it is a mixture of hydrogen sulfide with various acids and amines, presumably split from the amino acids of the protein.

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Monosodium glutamate appears to be entirely without odor when pure. Its taste has all four components: sweetness, sourness, saltiness and bitterness. In addition, glutamate has the capacity for stimulating the feeling nerves of mouth and throat to produce the sensation describable as "satisfaction."

Amino acids in general, as well as their sodium salts and their hydrochlorides, appear to be without odor. The taste of those in the neutral range of pH seems always to be sweet but usually somewhat bitter. Saltiness and sourness, which characterizes glutamic acid and its sodium salt, are exceptional tastes among the amino acids.

It is concluded that since meat flavor is predominantly odor, and pure monosodium glutamate is odorless, that meaty flavor cannot be due to, or be reproducible by, monosodium glutamate. The origin of the meaty association has been traced back to the crude glutamates formerly available, which had odor, due to protein decomposition products.

When monosodium glutamate was first produced in Japan a generation ago, it was claimed by some to produce a meaty flavor. Its developer, Ikeda, however, was more cautious and explicit and said that it had a "glutamic taste," implying that this was something new among tastes. The meaty association may have been mostly wishful thinking, for meat was a scarce and much-appreciated food, or again the claim may have been allowable within the limits of advertisers' license. At any rate, the thought that glutamate had a meaty taste came to this country along with the glutamate, and that thought still persists. Some users call glutamate "chickeny" rather than meaty while still others deny all meaty association.

In a ten-year study on "The Flavor of Meat and Meat Products" made by the United States Department of Agriculture and reported by Howe and Barbella in 1937, some tests were run on purified monosodium glutamate to find out if it were responsible for the flavor of meat. A negative conclusion was reached. To quote, "this recrystallized material has been offered to judges in solution of high molarity and also in dry form, and meat flavor has not been associated with them. It is our belief that this alleged meat flavor, if present in the original compound, must be due to the impurities present rather than to glutamic acid or its monosodium salt."

Recently, studies have been carried out at the Arthur D. Little laboratories on the flavor of meat and also on the flavor of monosodium glutamate and various amino acids, using a panel of tasters. We report herewith the highlights of the findings. For the benefit of those who may wish to go into more detail than is practicable in this paper, our studies will be published shortly as two papers, in *Food Research*.

The Flavor of Meat

In our work on meat, we sought to find what constituent of meat gives rise to flavor in cooking and to gain some idea of the nature of the flavoring substances produced. This was done on beef, then on

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pork and lamb and finally on chicken. Unaged meat was used to avoid bringing in the factor of "ripening." The cooking done was always gentle, at or below 100°C. to stimulate conditions inside a roast or other sizeable piece of meat. That procedure and objective proved adequate for the present study, and pyrogenic flavor development such as occurs on the browned outside of the roast, steak or chop was left for a later study.

The first testing was carried out to determine whether juice or fiber was the source of the flavor of cooked meat. Some fresh beef of good quality was trimmed of all localized fat, it was pounded, and then was squeezed in a hydraulic press to remove the bulk of the juice. The light gray mass of squeezed fiber was then leached in cold water for several hours to remove juice not squeezed out by the press. The fiber mass was found to be odorless and tasteless, though on chewing it was found to produce a slight feeling of astringency in the mouth. On being heated even to 50°C. appreciable odor developed. This was most easily detected by chewing a piece of the warmed fiber, whereby the structure was opened up and the aroma diffused into the smelling area of the nasal chamber. After being heated to 100°C. for an hour, the fiber became strongly "meaty" and could be smelled directly by the nose from an appreciable distance. It was the "cold roast beef" type of odor, sulfury yet pleasingly fragrant. On chewing, it tasted meaty but the effect was found to be due almost entirely to aroma since it vanished when the nose was pinched.

Some juice freed of fiber was then smelled and tasted. It had weak serum-like odor of the piperidine type. It had considerable blood-like taste, in which saltiness and sweetness were distinctly evident. On being heated, this juice coagulated. It developed almost no aroma, and the taste was found to be not much different from what it was before the heating.

Fat was then smelled and tasted, raw and after heating, and likewise bone and marrow. In no instance was there appreciable meaty odor or taste, originally, or on heating.

These simple tests proved that the odor and taste of raw meat reside mostly in the juice, whereas those of cooked meat come from the fiber. Also, it was shown that the distinctive flavor of cooked meat is predominately odor.

Pieces of beef were then boiled, in plain water, in acidified water and in alkalinized water and the odors evolved were noted. Other tests made, wherein the vapors from beef were condensed by boiling in a Claisen flask, proved that hydrogen sulfide was given off and was an important constituent of meat flavor. Acidic substances were found to be evolved but were not identified in the presence of the hydrogen sulfide. Alkaline vapors included a simple low amine such as a methyl-

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amine, a piperidine-like amine and probably, indole. The combination of these unpleasant substances plus possibly some neutral substances constituted the relatively pleasant odor that we know as "meaty." Since these substances were produced from fiber, which is principally protein, one might speculate that they were protein fragments, presumably produced by thermal "cracking."

Glutamic Taste

The writer, in 1932, in cooperation with L. F. Henderson, studied the taste of purified glutamic acid and its monosodium salt. We sought at that time to analyze the glutamic taste, to find out if it had some unique characteristic which made it exceptional among tastes. We made up solutions of sugar, salt, tartaric acid and caffeine and combined these in various ways in the attempt to match the taste of sodium glutamate. At about 2 thresholds of concentration of glutamate, we were able to match its taste rather well with 0.6 threshold of sweetness, 0.7 of saltiness, 0.3 of sourness and 0.9 of bitterness. At that time we felt well enough satisfied with this match that the glutamic taste was considered as operating only through the usual four kinds of taste buds.

Today, we find a "tingling feeling" factor in addition to taste. Besides the tingling feeling there is marked persistency of taste sensation. The persistent effect is present in the whole of the mouth region, including the roof of the mouth and the throat. It is difficult to describe this sensation other than to call it a "feeling of satisfaction."

What can be the cause of this glutamic effect, which is apparently independent of true taste, but which adds psychologically to the flavor of whatever has been eaten? It is suggested that monosodium glutamate may act as a functional amine which reaches and stimulates nerve endings lying within the buccal cavity. If so, this effect should be expected to be highly specific as to molecular constitution, with isomers and homologs mostly inactive, as is the case. In any event, it is proper to consider glutamate as a stimulator of the sense of feeling as well as that of taste, and the indications are that it is unique in this capacity.

Studies of Purified Glutamate

Glutamic acid has been freshly purified by a combination of carbon treatment and recrystallization to produce a fine white meal nearly or completely free from odor. This has also been done with its monosodium salt, leading to the conclusion that these pure substances have no odor.

When odoriferous lots of monosodium glutamate were treated in water solution with activated carbon, much of the impurity was adsorbed by the carbon, leaving the glutamate with much less odor. When the used carbon was washed free of glutamate solution it was observed

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to give off considerable odor, implying that the adsorption was at least partially reversible. When the carbon was treated with acids, the adsorbed acids were released in considerable amount from the carbon and the bases were suppressed. When treated with caustic alkali, the bases became conspicuous and the acids were suppressed. The acidic odors released were sourish and caramel-like, suggesting caproic acid. The basic substances evolved were numerous, including a simple amine, piperidine, indole and a substance of plastery-earthy odor. Whether these substances were derived from the glutamic radical or from associated impurities is not known, but chemically they could have been derived from amino acids by "cracking" or by some other type of disintegration.

Pure odorless sodium glutamate has considerable taste value, detectable in concentrations as low as .03%, strong at .5%, but not apparently much stronger at greater concentration. By direct observation, the taste of solid glutamate appears to be only salty and sweet, whereas in solution all four components are obvious.

The taste of glutamic acid is reminiscent of that of sodium glutamate, but is much sourer. It has not been observed to produce any marked feeling reactions. As an acid it is about as sour as the same concentration of tartaric or citric acid. The pH of glutamic acid is about 3.3 and that of monosodium glutamate, 7.0, in concentrations of about 0.2%, such as might be used in foods. A titration curve between these points is of a smooth sigmoidal type with no evidence of intermediate compounds. Since the pH values of almost all foods in which glutamate is used fall between these two points, it is probable that both the mono-acid and di-acid glutamate ions (HG^- and G^{--}) are present. Due to the great buffering action of the saliva and of the tissues of the tongue, we get the glutamate taste whether glutamic acid or its monosodium salt is applied to the taste buds and therefore we cannot tell from direct observations which ion is responsible for the taste. We vote for the mono-acid ion in view of what is now known, but the grounds for choice are not too secure.

Amino Acids other than Glutamic

Examination of over a dozen amino acids of high purity, including methionine, have led to the conclusion that amino acids in general as well as their sodium salts or their hydrochlorides are without odor. Studies of the tastes of these acids were also carried out. Most of the amino acids, unlike the doubly-acid glutamic, hydroxy-glutamic and aspartic acids, gave solutions that were chemically neutral or nearly so. Where this was the case, the acid itself was used; where not, its sodium salt. Three amino acids were found to be conspicuously sweet-tasting: glycine, alanine and hydroxyproline. Nearly every other one

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tested, again including methionine, was weakly to moderately sweet. It seems that sweetness of taste is a characteristic of amino acids. No saltiness of taste was noted except as previously recorded with the sodium salt of L (+) glutamic acid, so that saltiness is exceptional tastewise. Sourness likewise was found to be rare and to characterize for the most part only the dicarboxy acids and the hydrochlorides. Many amino acids were found to be bitter to some degree though none were strongly so. Bitterness in slight degree may, therefore, be considered as characteristic of amino acids. The sodium salts of the two aspartic acids, and of the D (—) glutamic acid were found to be tasteless or nearly so.

To the best of our information, the taste of L (+) glutamic acid and its monosodium salt is unique: a relatively strong taste composed of a blend of sweetness, saltiness, sourness and bitterness with a persistent tingling feeling remaining in the mouth.

The Flavor of Meat versus the Taste of Glutamate

The typical or characteristic flavor of cooked meat, as determined by direct test, has been found to consist of aroma produced by the action of heat on meat fiber. This is true of all kinds of meats including chicken. The taste of meat is slight compared with the aroma, this taste resides in the juice, and it is not significantly affected by the operation of cooking. Meat flavor is principally smelled rather than tasted.

Pure glutamate has taste but essentially no odor. In this fundamental respect it cannot substitute for meat. It is not meaty, or chickeny, and the reason for its successful use in food must be sought in some other direction.

The association of early lots of glutamate with meatiness can now be ascribed principally to the strong odor of the crude glutamate then available. The pure glutamate commercially available today is not meaty; yet it has greater value in foods, in reinforcing or accentuating their natural flavors than the old odoriferous glutamate.

References: (15) (16) (33) (35) (41).

Discussion

Dr. Crocker: The temperature in the interior of a large roast of meat never exceeds the boiling point of water. The temperature reaches 140°F. for a very rare roast, and up to 180°F. for a well-done roast. The actual cooking temperatures within the body of a piece of meat are relatively low. When you chew articles that are very low in odor, you release the aroma, it goes up to your smelling chamber by the back way and is detected. It is always interesting to find out whether odor alone is present or just taste. You pinch your nose, and at the point

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of release if flavor appears in a greater amount, then it is only aroma.

Dr. Manning: Does the temperature inside a roast of beef and the length of time of cooking destroy the enzymes that would hydrolyze the proteins in the beef?

Dr. Crocker: The answer to that question is that there are no enzymes apparently involved in the production of meaty flavor. That is treated in detail in a paper to appear in *Food Research.*

Mr. Galvin: On this soluble or liquid fraction of meat, have you done any analytical work which would indicate what the meat flavor is due to in any of these soluble fractions?

Dr. Crocker: No analytical work has been done by us. I wonder if the Meat Institute has done anything on that problem?

Dr. Kraybill: None.

Dr. Anson: In confirmation of this idea that the taste of meat is aroma, you can take cooked meat and distill it and the flavor will be distilled off. One can get very complicated in talking about analysis of taste, but if you take an ordinary person and give him a mixture in the right concentration of glutamate and salt, he is reminded of meat or chicken. What it means in a more profound analytical way, I would not know.

Dr. Manning: Would taste tests carried on in that way with articles of food left in the mouth cause that effect, or should tests be carried out by a jury in which the teeth have been cleaned by a dentist?

Dr. Crocker: We went through a great deal of effort with a few people to find out if the condition of the teeth had anything to do with it, and the conclusion was quite negative. We found also that the saliva had very little to do with it.

Mr. Nair: In connection with this question of whether glutamate has a chicken flavor we tried out a taste panel using dried chicken meat and salt versus glutamate and salt. The powder dried from chicken broth and chicken meat was suspended or dissolved in water with a definite concentration of salt (about .7%). Glutamate was dissolved in water with the same salt concentration. At low levels of flavor concentration some people identified the glutamate solution as having a fairly good chicken flavor while other panel members were uncertain whether the chicken meat suspension had a chicken flavor or not. Of course we had to cross them up a bit so they did not distinguish between the samples by observing differences in clarity of appearance. I might add that we always test such solutions with salt present to bring out glutamate or chicken flavor. We incline to the view that some people identify glutamate as chicken-like in flavor.

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The Effect of Monosodium Glutamate on Food Flavor

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Author's abstract

Studies have been made to determine the role of monosodium glutamate in food flavoring. While some observers assert a meat-like taste for monosodium glutamate, we have found it to have only a sweet saline taste accompanied by some astringency. It appears to have a notable and usually favorable effect on food flavor by blending and rounding out the notes without contributing any noticeable odor or taste. This improvement in flavor appeal was most notable in the case of meats, seafoods, stews, soups and chowders. Many vegetable dishes developed added attraction by addition of glutamate. It was noted that glutamate suppressed undesirable flavor factors in some cases. Glutamate also aided in combating over-cooked flavor often noted in steam table food. Fruits, fruit juices, sweet baked goods, some dairy products and cooked cereals were not considered to be benefited.

Attempts to determine the relative effect of pH on glutamate effect in a single food were unsuccessful as changing pH produced flavor changes greater than those produced by glutamate. Glutamate appears to be effective in the pH range investigated, 3.5 to 7.2, the limits being represented by certain tomato products and hominy.

Monosodium glutamate accentuates sweet and salty tastes in food when they are present in less than optimal amounts. In some cases, glutamate seems to suppress sourness and bitterness. Glutamate has more influence in fat-free foods than it has when fat is present.

The flavor of food is composed of many different notes, which together make up a flavor "profile." This profile is determined by combining the impressions of the members of a taste panel, and allows a means of studying the effect of added materials without regard to individual preferences. A seasoning accentuates desirable notes and suppresses objectionable ones in food without itself being evident. For this reason, monosodium glutamate may be classified as a seasoning agent; its unique action being more of a salt than a condiment type. Because of its importance and the fact that it can effect the balance of other seasoning and flavoring, it should be added first.

Although monosodium glutamate has been available for many years, the literature on its fundamental role in food flavoring is extremely limited. No published work supplies a general theory to explain its action or to define its place in the field of salt, spices and seasoning. It has frequently been referred to as a material having a meat-like flavor but this viewpoint has also been contradicted.

Our work on monosodium glutamate was initiated over a year ago with the purpose of answering some of the questions which have arisen in connection with its use through the development of a background of information on its mode of action and general effect on food flavor.

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Results of these studies will be published soon in *Food Research* and *Food Industries*, and the two papers being presented today are drawn in part from articles already submitted for publication. The following is a list of the principal topics studied:

1. General orientative study of monosodium glutamate in sixty different cooked foods.
2. Taste and flavor evaluation of highly purified MSG, commercial MSG, isolated impurities, D- and L-glutamic acids.
3. Taste evaluation of MSG at food levels in the range of 0.1-.0.3%.
4. Taste and flavor evaluation of common meats.
5. Effect of MSG on fundamental tastes (sweet, salty, sour and bitter).
6. Effect of MSG on aromatic components of flavor.
7. General relationship of glutamate effect and pH.
8. Influence of thickening agents, fats and related materials on glutamate activity.

General Observations

When tasted in Nuchar-treated water at food levels of 0.1-0.3%, commercial monosodium glutamate had a sweet saline taste accompanied by some astringency. It stimulated all surfaces of the tongue and oral cavity, producing a slight sensation of "furriness" on the tongue. A mild but lasting aftertaste resulted. Solutions were almost odorless and therefore at these concentrations MSG would be expected to contribute only sweet salty taste to food flavor.

Monosodium glutamate added in small amounts had a pronounced effect on the flavor of practically all foods to which it was added, without itself being noticeable. (Exceptions: It was very noticeable in certain fruits and dairy products.)

Under the same conditions glutamate had an effect on food aroma, without contributing any noticeable odor itself. (0.1-0.3%)

The principal effect on food flavor was a balancing, blending and rounding out of total flavor.

Flavor appeal was frequently improved, most notably in the case of meats, seafoods, stews, soups, and chowders. These are applications with which you are most familiar.

Cooked vegetables were markedly improved by glutamate addition, but the following were highest on preference rating: mushrooms, sweet corn, asparagus, broccoli, green and lima beans, spinach, cauliflower, brussels sprouts, squash, parsnips, onions, and dehydrated cream style vegetable soups. In carrots and cauliflower the natural flavor characteristics were intensified. This result suggested application of monosodium glutamate in protecting the flavor of foods held on steam tables.

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For example, in canned corn, canned lima beans, and dehydrated and reconstituted vegetables maintained for more than an hour over a hot water bath, monosodium glutamate aided in combating steam-table flavor.

Fruits, fruit juices, sweet baked goods, some dairy products and cooked cereals were not considered to be benefited by use of MSG.

It was noted that glutamate suppressed undesirable flavor factors in the following cases:

1. The sharpness in onion flavor.
2. Rawness in many vegetables and some meats.
3. The flavor of peel and earthiness in vegetables, particularly potatoes.
4. A volatile characteristic note in boiled rice.
5. Bitter tastes in a few freshly opened canned vegetables.
6. A fishy note sometimes present in lima beans.

The Effect of pH

Glutamate has been investigated in foods in the pH range 3.5 to 7.2. A taste titration curve indicated that glutamate taste was notable throughout this range, and was accentuated at the lower values of pH. The foods in which the effect was most desirable happened to lie in the range pH 5.5 to 6.5. Attempts to determine the influence of pH on glutamate effect in a single food were, however, unsuccessful. Changing the pH of chicken broth by as little as ± 0.5 units produced flavor changes greater than those produced by glutamate. These unfavorable changes greater than those produced by glutamate. These unfavorable changes were not corrected by adding glutamate. However, our general observation was that glutamate was effective in the pH range of 3.5 to 7.2, the limits being represented by certain tomato products and hominy.

We are intrigued by the apparent intensification of glutamate taste in the more acid solutions and feel that more work should be done on the relationship of glutamate taste to glutamate effect at various pH values.

Effect of Demulcents and Fats

Observations made on aqueous solutions and dispersions of flavoring agents do not correlate exactly with those found in food. Foods generally have higher viscosity and usually contain fats and oils. These factors markedly affect the balance of a flavoring system. Consequently we have begun a series of studies on the fundamental taste factors in thickened non-food media. Using one per cent solutions of carboxy methyl cellulose we have observed a pronounced demulcent action, by

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which sweet, salty, sour and bitter tastes and the effect of low concentrations of glutamate were suppressed. At higher concentrations taste seemed to be more pronounced and longer lasting. At higher concentrations of glutamate, bitterness and sourness were suppressed. Well seasoned non-meat gravies were prepared with cereal thickening agents with no added fat, and glutamate was found to improve their flavor. Addition of fat suppressed all flavor, requiring development of a new seasoning and flavoring at a higher level. Glutamate effect in this system was less pronounced than in the case of the non-fat gravy.

Effect of MSG on Sweet, Salty, Sour and Bitter Tastes

In examining fundamental tastes we have found that glutamate accentuates sweetness in a food when sweetness is low or near optimal values. When sweetening was optimal, glutamate had no great influence. The same applied to saltiness. When farina or mashed potatoes, for example, were salted with 75% of the optimal amount of salt, 0.1-0.2% MSG could supply the remainder. Glutamate alone could not supply adequate salt value to these foods.

Tests with plain water indicated that glutamate appeared to be more salty than salt at 0.1-0.2% levels (subthreshold levels of salt) but at threshold levels glutamate added some saltiness to the salt solutions. Above threshold, the saltiness of salt solutions was not greatly increased by adding MSG.

Sourness accentuated glutamate taste. Glutamate seemed to suppress sour taste and odor in certain vegetables but not by affecting pH.

Glutamate appeared to suppress bitterness in saccharin solutions and in certain vegetables, but this action was not general.

The Philosophy of Seasoning

As a prerequisite to classifying monosodium glutamate among common seasoning and flavoring agents, we have attempted to find objective data on how salt, pepper and spices react upon food flavor. A review by Dunn (17) on the flavor effects of salt and original work by Fabian (21) and Blum supply some understanding as to the complex possibilities with salt, sugar and acids. Similar background on spices and condiments is lacking. Some speculation as to the general philosophy of seasoning is possible from our work with monosodium glutamate and it is presented here, tentatively, with the idea of suggesting approaches to the problem.

In attempting to make objective measurements on flavor effects one is handicapped by the usual limitations of subjective impressions, preferences and prejudices, especially in dealing with food. Our approach has been to conduct an open panel discussion to determine the principal notes or points of odor and flavor on the unseasoned food. A

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composite of these points is called the odor or flavor profile. Subsequent observations may then be made on the effect of an added ingredient upon particular aspects of the profile, without reliance upon preference.

Spices and condiments were said to have been used originally to suppress objectionable unsavory flavors in spoiled meats. Why then are they necessary in modern cooking? Our observations indicate that unseasoned food generally has a sharp open profile with many notes individually evident. Such flavor lacks blending and balance. Cooking makes for notable improvement in character but still leaves rawness and sourness, particularly in vegetables. Salting is the first step in correction of rawness and other objectionable flavors may be controlled by sugar, acid, pepper and flavoring agents.

Seasoning is the art of making fit; it has much to do with palatability and appeal. Seasoning can be accomplished without the additives being noticeable. Bizarre or outstanding notes may then be added for special effects but this is a step beyond minimal seasoning requirements. Seasoning increases total volume of flavor and although it may suppress some outstanding notes of natural flavor it does not destroy identity. Some parts of the natural flavor profile may be accentuated and others suppressed; a good seasoning accentuates the desirable notes and suppresses objectionable ones.

We believe that monosodium glutamate should be classified as a seasoning agent since its action is more of the salt type than the condiment type. Because it can effect the balance of other seasonings it should be added first. When used judiciously it is not apparent in cooked foods and its effect is not duplicated by any other seasoning agent. It can still give zest to a food after all of the recognized art has been applied.

References: (17) (21).

Discussion

Dr. Fellers: In regard to canned products, have you determined whether processing, such as you would use with process meat, corned beef hash, clam chowder, etc., affects the monosodium glutamate flavor? Does it change the blend of flavor or destroy the fullness?

Dr. Cairncross: In our work we have not dealt with the food technology aspects of canning procedures, etc. Our work has been done on fresh vegetables and freshly prepared dishes.

Mr. Galvin: With reference to canned soups, the glutamate taste is not very much affected by ordinary heat processes. You will find, I think, that other flavors of foods—flavors of carrots, peas and corn—will change a greater amount than will the glutamate.

Mr. Stateler: In vegetable soups where potatoes are an ingredient—too

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the overall volume of flavor. In Farina for example, we observed the blending of natural flavor and suppression of sourness and rawness. By glutamate effect we mean that overall effect on flavor which occurs and which is not predictable from addition of the known spectrum of the glutamate taste. We believe that that effect includes the sensations produced in the mouth—possibly salivary stimulation and other factors which we have not as yet analyzed. We mentioned that the aroma of the food is generally affected by glutamate, and often with the highly purified glutamate added to the cooked food there is a marked difference in odor appeal.

QUESTION FROM THE FLOOR: Would you say a few words about the comparison of the D and L forms?

Dr. Cairncross: We have done very little in comparing the two forms of glutamate except as Dr. Crocker mentioned the glutamate taste is characteristic only of the naturally occurring form and the glutamate effect is characteristic of the same form. We have not done any extensive food tests with the two isomers except to confirm the fact that the taste was predominantly common to the L-plus glutamic acid.

Dr. Anson: The unnatural form is not devoid of taste, and the taste is not completely different from that of the natural form. It is considerably lower in taste, but not enough to be negligible.

QUESTION FROM THE FLOOR: Is there much difference whether glutamate is added during cooking or just before serving?

Dr. Cairncross: Experiments with processing would give us a better idea on that. We often prefer to cook glutamate with the food in order to get it well blended with the food. I would say it would be more desirable to cook it into the food. I cannot predict whether there would be any great economy or practical gain thereby.

Dr. Shannon: Regarding the canned taste that was mentioned with canned foods, maybe some of you have tasted Oscar Mayer's product, wieners with barbecue sauce in a separate sack. The reason behind that is to mask the canned flavor, and we have masked that fairly well.

QUESTION FROM THE FLOOR: I wonder if you have noticed anything in green vegetables. Have you tried preservation of color?

Dr. Cairncross: There may be small difference in preservation of natural color, but in our experience the effect is not to be compared with that obtained with bicarbonate or some other device.

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often in these soups when canned, there is a sort of staleness in the flavor of the potatoes. If glutamate is present or is added to the soup, will that staleness be dispersed?

Dr. Cairncross: We have observed that glutamate in freshly opened canned goods frequently suppresses an undesirable note that was apparent on canning. In the case of canned bean sprouts and in the case of a number of other vegetables, there is often a correction of an overcooked or undesirable flavor.

Mr. Sjostrom: We did some work on canned potatoes and noticed a decided cut-down on earthiness. Earthiness is associated with the flavor of the peel which develops in canned potatoes. It is also tied in with overcooked flavor. Glutamate when added to these potatoes did improve palatability.

Dr. Cairncross: We also had limited experience with dehydrated potatoes.

Mr. Sjostrom: Several years ago when we were getting into some of the dehydrated work, we attempted to use dried potatoes in dehydrated soups. One fault at that time was that potatoes were not stable over long enough periods. The glutamate, however, did add something to the freshly dehydrated potatoes to make a better flavor.

Mr. Bauer: Our type of investigation has not been along this line.

Dr. Melnick: One of the major problems facing the Institute is canned meat flavor. I wonder if glutamate is capable of masking that taste.

Dr. Cairncross: We have done very little work in that connection. We have taken it for granted that glutamate fits in with meat preparations in general, and we agree that it supports the flavor of any meat dish or animal protein preparation, but we have used vegetables primarily because we get a greater range of complex flavors.

Dr. Buchanan: In your paper you discussed very briefly glutamate taste versus glutamate effect; I wonder if you have done enough with the advantages of glutamate in prepared foods to comment further, and particularly, on what you meant by glutamate taste versus glutamate effect as far as concentrations of glutamate in food and preparation go. Can you tell us what you mean by glutamate effect?

Dr. Cairncross: We think of food flavor as a sort of pin cushion model, an open profile with many characteristic points easily discernible, such as sour, sweet, bitter and astringent notes. We know the spectrum of glutamate very well. If we superimpose that upon a food flavor we can predict what it will add to the spectrum of the whole flavor. When we add glutamate to food we do not observe a simple additive flavor effect but we have observed major changes in the flavor profile and in

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The Taste of Monosodium Glutamate And Other Amino Acid Salts in Dilute Solutions

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Author's abstract

Observations were made on simple systems involving monosodium glutamate with the object of learning a few elementary facts about its usefulness in the absence of highly complex flavoring systems of ordinary foods. Glutamate in distilled water at concentrations from 0.05% to 1.0% is just slightly sweet and slightly salty. No usefulness would be ascribed to glutamate from this experiment. Glutamate with salt produces a taste that is mildly sweet and pleasantly salty, but having an additional effect of an apparent high flavor intensity. This flavor is obviously useful. Increasing concentrations of glutamate require increasing salt concentrations for strongest glutamate taste. At low glutamate concentrations saltiness is diminished.

Glutamate taste is affected by pH. Maximum taste is noted between the ranges pH 6 and 8. Taste diminishes slightly at pH 5 to approximately 80% of original intensity. Greater reductions are apparent at pH 4 and 3.3.

These experimental results obtained by working with simple systems would indicate that in applying monosodium glutamate to foodstuffs, particular attention must be paid to the salt content, the pH of the food and the sweetness. All may require adjustment to achieve the maximum benefits of the glutamate.

Solutions of 20 different amino acids (some L, others DL- form) were tasted in 1% salt solutions at pH 7, in concentration equivalent to .5% monosodium glutamate. Most of the amino acids had very slight taste, usually sweet, although a few were markedly sweet. None had any ability to produce a useful glutamate-like taste. A few of them may have some useful flavor applications when tested under different conditions.

The usefulness of monosodium glutamate for improving the flavor of a variety of foods has been known for a number of years. Other papers on today's program deal with its application in a number of specific uses. The fact that it is valuable in products of noticeably dissimilar taste characteristics has often led people to attribute to it a chameleon-like ability to change its taste to match its taste environment. Whatever the mechanism for its usefulness in this variety of foods, the subject is certainly worthy of considerable study.

During the course of the last few years, I have made a number of observations of glutamate in simple systems with the object to try to learn a few of the elementary facts in the absence of the highly complex flavoring systems of ordinary foods. These observations are offered here, not as an explanation of the glutamate effect, but to promote discussion and to suggest further study along these lines.

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The simplest experiment with glutamate is to add it to distilled water in various concentrations ranging from 0.05% up to 1.0% in small increments. The lowest percentage observed gives a taste noticeably different from the distilled water. The taste is one of a pleasant sweetness which increases with the concentration. The slight sweetness is somewhat greater than equal percentages of sucrose at the low levels. The flat taste of distilled water is diminished even by the lowest levels used, and a slight saltiness develops with increasing concentration, so that at 0.5% glutamate there is a saltiness which could be rated approximately equal to an 0.25% sodium chloride solution. The only unusual taste effect is the persistence of a sweetish character which is perceptible in the mouth for periods longer than one-half hour. Observations made on such solutions indicate merely that glutamate is a pleasant tasting substance with considerable persistence. One would scarcely ascribe any useful taste quality to it. Undoubtedly this is the reason that glutamate was known as a chemical compound for about fifty years before any useful character was noted.

However, most foods are eaten with appreciable amounts of salt being present. If we examine a solution containing 1.0% salt and 0.5% glutamate, we will find that the taste is as mildly sweet and pleasantly salty, but there is an additional effect of an apparent high flavor intensity somewhat difficult to describe inasmuch as it is not identical to the high intensity of too sweet sugar solutions or too salty salt solutions. Rather, it seems that all the taste buds are stimulated pleasantly and the stimulation persists for a long time. The closest similar taste I know is that of a salted chicken broth, although the broth is lacking in this high intensity factor. This taste is obviously *very useful* and from here on, I shall refer to it as a normal glutamate taste.

Having noted that salt plays a very important role in the glutamate effect, a series of observations have been made in which the glutamate concentration is varied between 0.05% and 1.0%, while the salt concentration is varied from 0.25% to 1.0%. At the lowest salt level, glutamate concentrations from 0.05% to 0.25% have noticeable normal glutamate tastes. As the concentration of glutamate is increased (still maintaining low salt level) to levels of 0.5% and 1.0%, a distinct sweetness becomes very prominent and the normal glutamate character is overshadowed. When the concentration of salt is increased to 0.5%, the normal glutamate effect is present throughout all concentrations of glutamate observed, but in the highest level (1.0%) additional sweetness is detected. With salt levels at 1.0%, the lower concentrations of glutamate have a normal glutamate taste, and the saltiness of the solution is materially diminished. However, when 1.0% glutamate is used, no reduction of saltiness is noted although the glutamate taste is a normal one. These observations indicate:

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1. That salt must be present to produce a useful glutamate taste.
2. That for optimum efficiency and palatability, the concentration of the salt is dependent upon the concentration of the glutamate.

The marked sweetness observed with the low salt—high glutamate solution does not appear to me to have useful application inasmuch as sugar is probably as suitable and less costly for this use. However, further experimentation may find some particular application of this property.

Since the pH of foods varies rather widely, observations were made to learn the effect of pH on the normal glutamate taste. Solutions of glutamic acid equivalent to 0.5% monosodium glutamate were made up in a 1.0% salt solution and adjusted to the following pH's: 3.3, 4, 5, 6, 7 and 8 with sodium hydroxide. The solution at pH 8 had essentially the same taste as the control (pH 7) except that a slight flatness was noted.

At pH 6, again, the taste was essentially identical with the control. However, at pH 5, the normal glutamate taste was noticeably reduced to approximately 80% of the original intensity.

The glutamate taste at pH 4 was even more reduced, although here the acid sourness itself was becoming rather prominent, so as to overshadow the glutamate taste.

Similarly, at pH 3.3, the glutamate taste showed even greater reduction.

These observations indicate that glutamate is more economically used at more neutral pH's.

In all cases, the aftertaste was the same as from neutral solutions. Apparently, the gradual return of the saliva to a neutral condition restored the original taste characteristics. The diminishing of the glutamate taste with increasing acidity suggests that it is affected considerably by the ionization of the second carboxyl group in the molecule.

These experimental results obtained by working with simple systems would indicate that in applying monosodium glutamate to foodstuffs, particular attention must be paid to the salt content, the pH of the food and the sweetness. All may require adjusting for achieving the maximum benefits of the glutamate.

The usefulness of glutamic acid salts as flavoring materials suggests that possibly other amino acids occurring in nature might also have similar properties.

Today, most of the twenty-odd naturally occurring amino acids are available in sufficient purity for conducting small scale tests. A few of them, however, are available only as a DL mixture. In preliminary tests on amino acid solutions no salt was included, and observations were difficult to carry on because of the unnaturalness of the distilled water

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taste. Consequently, 1.0% sodium chloride in distilled water was adopted as the standard. In all cases, the pH of the solution was adjusted to 7.0 before tasting. The concentration of each amino acid was equivalent to 0.5% monosodium glutamate.

The DL alanine solution simply had a sweet taste with no other interesting characteristics.

The L (+) arginine had a slightly sweet taste, and it diminished the salty taste somewhat.

Both L (+) aspartic acid and its DL form had a slightly sweet taste, and a very weak glutamate character. However, I did not feel that its glutamate character was sufficiently interesting for commercial use.

The L (—) cystine merely had a slight sweet taste.

Glycine was rather strongly sweet and the saltiness was somewhat reduced.

The L (+) histidine solution was somewhat more salty than the control. It had a slight sweet taste, and also a slight sourness, which is hard to explain in conventional terms since the pH was neutral.

The L (—) hydroxyproline solution was sweet with a rather pronounced bitterness suggesting a burned taste.

Both L (—) leucine and DL isoleucine were slightly sweet and had very slight bitter aftertastes.

The L (+) lysine had a mild sweet taste and a suggestion of glutamate taste although, again, not enough to be of commercial interest.

The DL methionine had a definite sweetness equivalent to about a 2.0% sucrose solution, but it also was slightly bitter.

The DL norleucine was also definitely sweet and exhibited considerable persistence in taste.

The DL norvaline and DL valine were just slightly sweet.

The DL phenylalanine was very sweet, perhaps as sweet as a 5.0% sucrose solution. However, a bitterness was very noticeable so the combination of sweet and bitter was somewhat reminiscent of a chocolate flavor.

The L (—) proline was just slightly sweet.

The DL serine and DL threonine had almost no effect on the flavor of the salt solution.

The DL tryptophane was very sweet, approximately as sweet as a 10.0% sucrose solution. There is an interesting point relating to taste and chemical structure because saccharine has a ring structure somewhat similar to tryptophane.

The L (—) tyrosine had a very slight taste.

From these observations we see that most of the amino acids are pleasant tasting substances which hold no interest as materials for pro-

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ducing a glutamate taste. A few of them may have some useful flavor applications when tasted under different conditions.

In commercial food practice today mixtures of amino acids in the form of protein hydrolysates are rather widely used as flavoring materials. With the simple experiments we have performed so far, it has not been evident that the flavor of these hydrolysates is mainly due to their amino acid composition. It appears that the reaction products undoubtedly involving carbohydrates, protein materials and perhaps other trace materials contribute largely to the flavor and aroma of the protein hydrolysates.

Discussion

Dr. Crocker: First of all, I am amazed at the closeness of conclusions of two independent workers. Second, as to the taste versus the effect of glutamic acid. Quite a few of the amino acids have taste of course, but only apparently the L-glutamic acid has glutamic effect. Another point brought up a little earlier in the meeting was with reference to saliva acting on amino acids. I found working with methionine that when you put it in your mouth it has only a sweet taste, but after 15 or 20 minutes it develops a very cheesy flavor and there the saliva has protein-splitting action. If you have only odor to a thing, such as in the case of roast beef, that is not too pleasant, so you put on salt and entertain another set of taste organs—you entertain the organs of taste with salt. It appears that glutamate is successful not because it adds taste, but because it adds feeling. When you can entertain three of your senses in flavor, you are playing a strong cord.

Dr. Gephart: You mentioned that one of the amino acids had a chocolate flavor. At what concentration was this apparent?

Mr. Galvin: Phenylalanine was characteristic of chocolate. It was made up to the equivalent of .5 percent monosodium glutamate in salt water, and the pH was adjusted to 7. It was quite sweet, and had a little bitter connotation thought to be reminiscent of chocolate.

Dr. Anson: It is presumptious to add anything, but I would like to say just a little bit more about the taste of amino acids. Some of them seem to be much more pleasant than others. I compared some protein hydrolysates, and I thought I would be able to predict from the amino acid of the protein what the hydrolysate tasted like, but I was not. I think that illustrates a very practical point. Unless you are a very experienced expert, the ordinary tester is quite incapable of synthesizing tastes or odors. The practical conclusion of that is that you are reduced to a very impractical approach. Unfortunately, that has been the history of flavoring.

Mr. Galvin: We have made experiments in the past which agree with

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Dr. Anson's observations on the difficulty of predicting what a complex flavor will taste like from a knowledge of the elementary flavors. Observations made on a number of protein hydrolysates made from wheat, corn, yeast, casein, and one or two others indicated that of all these proteins only the casein hydrolysate tasted something like we thought it should, whereas the others did not.

AFTERNOON SESSION

The Use of Monosodium Glutamate In Sea Food Products

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Author's abstract

Attention is called to the many types of protein hydrolysates on the market and to their great variability in content of monosodium glutamate, salt, ammonia, inert matter and moisture. Each product must stand on its individual merit and no conclusion can be drawn as to the suitability for seasoning foods of hydrolysates as a class. Generally, pure monosodium glutamate is preferred as a flavor improver for seafoods. It is a pure, standardized product and gives reproducible results. Usually, concentrations of monosodium glutamate of from 0.15 to 0.5% are best for clam and fish chowders, fish cakes, soups and purees. In pastes and sandwich spreads as much as one percent can be used. Canned oysters are improved by MSG but the flavor of shrimps is not enhanced in the opinion of some members of our taste panel. Anchovy and lobster spreads are markedly improved in flavor. Heat and processing change the flavor of MSG somewhat but do not usually produce off- or undesirable flavors.

Most clam chowders found on the U. S. market contained MSG. The latter does not appear to mask or cover up the odor or flavor of stale or partially decomposd seafoods. Monosodium glutamate showed no preservative value in seafoods.

The Japanese used monosodium glutamate and protein hydrolysates freely in their canned and dried Army rations such as canned fish and gravy and many meat-vegetable or soybean combinations which contained little meat.

When we started working with these hydrolyzed protein products a few years ago, looking for a way to enhance the flavor of some of the marine foods in New England and the East Coast, we got many samples of monosodium glutamate and the different hydrolysates in various stages of impurity and tried them out.

What is monosodium glutamate? Let us talk first about what are often passed off as glutamates and hydrolysates. It seems to me that

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is a rather important aspect of the subject, and I would like to present it for what it is worth—even though it may mean stepping on the toes of some manufacturers. But if these other products spoken of do have something, let us know what they have. The products we obtained included liquids, pastes, and powders; some were black, some white, and all colors in between were represented. They gave us quite different results, and I should like to emphasize what was said—that these products act differently, depending on whether they are in the presence of a little salt, a lot of salt or no salt, and also whether they are in a product like pickled herring with acid added to them. Acid also changes the flavor complex considerably.

These hydrolyzed proteins are really remarkable products. You have heard the discussion of what they do from Dr. Crocker and other speakers. You have heard their properties described in terms of Dr. Crocker's famous formula of salty, bitter, sweet, and sour. We did try these various flavoring agents in such products as salt fish and codfish cakes. We tried them on clams and clam chowder, on canned lobster and lobster paste, on crabs and crab cakes, and on gefüllte fish, a product that is canned to some extent in this country and liked by many people not of the Jewish faith. We tried them on some fish pastes, oyster stew, marinated herring, and anchovies. Some of these were already in a semi-fermented or decomposed condition and some, like our cheeses, are not exactly up to snuff as regards absence of decomposition, but the Food and Drug Administration does not offer much objection.

There is a degree of hydrolysis in some of these fish products already, due to bacterial action, and in some respects the flavor resembles these hydrolyzed proteins. In fact, that is what it is.

What concentrations did we use in these products? If you taste a product at about 1% salt, we don't think you can taste under .1% of monosodium glutamate. I suspect .05% is true in water or products which don't have much flavor. From there you can go to 3 percent. One of our speakers said that .5% gave you a maximum taste threshold and, if you use more, your curve does not go up. In other words, you don't get twice the flavor from adding 1% that you do from .5%.

We found that heat does affect monosodium glutamate and these hydrolysates, but not as much as it does the hydrolysates themselves. A canning process of 240-250° F. definitely does something to the flavor. In some cases it improves it; in some cases it makes it inedible. The only way to know is to try it out. I know of no way to predict what products monosodium glutamate is going to improve and which it is not. The field it covers and the products it does improve are certainly remarkable. I would not believe that the same product that could improve marinated herring with a 1 to 2% acid would also improve lob-

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ster paste or crab cake and codfish cakes, but it does. You have to use it with caution. You have to try it out, and I am sure there is a huge field there and we have hardly dented the surface.

For example, we put a little monosodium glutamate in canned oysters. They are not much to talk about and have never been too popular. If you put a little monosodium glutamate in them, it really adds something. It is the same with clam chowder. I don't know about the products of other industries, but it is being rather widely used in the marine industry. It is rather new of course and the method used is more or less hit or miss. Interest in this subject on the part of industry generally and others as well is shown by the number of people here and the many notables sitting in this audience. Its range of usefulness is great. The use of soybean sauce and Worcestershire sauce in so many of the English products—puddings, gravy products, etc.—suggests the diversity of products in which monosodium glutamate can be used. Whereas the English have perhaps used some glutamate in their fish products and pastes, it has not been done to any great extent as yet.

Some of the hydrolysates carry a very strong color, since some of them have caramel added. In marine products, that is generally unfortunate, because we want to keep the product as light as possible. I think for marine products we want to use pure monosodium glutamate. Neither do we want an excessive amount of salt, ammonia salts, or sodium chloride. There is no question but that monosodium glutamate carries its own salt, but it goes up to a certain point on the scale of salinity and then you don't seem to notice it. Most people like sea foods fairly salty. They think that everything that comes from the sea ought to be salty. Of course, a crab or shrimp is not any saltier than a fresh water fish. Again, when we add a lot of salt, we have to be careful about adding glutamate since we don't wish to overdo the saltiness. Excessive salt covers up the glutamate flavor. We have found that in a good many cases glutamate as a flavor factor seems to work much better in very lightly salted than in the more highly salted products. For example, salt codfish flakes are used in quite a few products. Glutamate does not work well in them, unless the salt content has been reduced somewhat.

I have just noted some of the satisfactory concentrations that we have found in some of these products: clam chowder—.1 to .3%—it does not make much difference whether added whole or mixed. We got so much variation with these hydrolysates that I would rather not talk about them. I have no objection to using them, but you can't tell what you are getting. Fish chowder—.1 to .3%; lobster paste or crab paste and fish paste—.5 to 2%. You can use quite a little in these pastes; it brings out the flavor nicely. In lobster and crab meat, we use the

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to remember—the original saltiness of your product makes a great difference in how you use this glutamate.

Somebody brought up the subject of soy sauce manufacture. I had a little personal experience making soy sauce by the enzyme method. It might be called a hydrolysate problem. There was a Chinese working in the Department of Agriculture about 1920, when I was getting out of school, and we worked together on making a soy sauce. He brought over what he called a greatly improved method. The method was to take about 50 percent soybeans (two varieties were used since some have a bad flavor and some good) and about 50% barley. These were soaked for two or three days and then sprinkled with a powdered mold, which he called "moyashi." It is very rich in enzyme, and soybeans and barley blended nicely with it. Then we put them in a room on shelves at 100 percent humidity. The mold grows through the beans and cereal, and by switching them around you have a culture through the beans and barley. Then you threw them into a barrel of salt, 10% brine, and stirred them up for a few weeks. The longer you store it, the better the soy sauce becomes. That is still the Oriental method. Practically the whole substance of the bean and barley goes into solution. If you siphon out this stuff after a year or so, you find very little sediment. The Chinese know the difference between good and bad soy sauce. Unfortunately the bad is often foisted off on us.

Evaluation of Glutamate In Food Specialties

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Author's abstract

The compatibility of glutamate with flavors present in any specific food under consideration is the first factor to be evaluated in determining the advisability of adding this seasoning to the product. As a general guide one should not expect glutamate to blend well with cereals, fruits, vegetables, or dairy products. It is a good adjunct for meats, fish, eggs, soups and gravies. Glutamate is usually a plus with salt or sweet flavors but not with acid or sour-tasting foods.

It must be remembered that glutamate creates a lingering, persistent flavor reaction and hence is not suitable in food or drink in which it is desirable to have an evanescent taste that disappears quickly. Coca-Cola, for example, would suffer in flavor appeal from the addition of glutamate. It has found its greatest application in intensifying chicken and meat flavors. Having decided that the food specialty to be seasoned can be improved in flavor by the use of monosodium glutamate, one then proceeds to determine at which level it will produce a desirable

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"tomalley" which consists of gelatinized protein in the body of the lobster and any eggs that are present. The eggs give a bright orange color to the paste. These are packed in Canada. Canada used to let England make up these pastes, but now they are packing them and so are we. Crab paste is a very fine spread indeed, especially with crab cakes and the gelatinized or heat-coagulated proteins that are in the body after you pick out the white meat. In smoked herring paste you can also use a pretty good amount of monosodium glutamate: 0.5 to 1.0%, usually around 0.75%. Until some years ago whiting was not utilized at all. The natives of New England would not eat it. But in St. Louis, where they like fish and chips, literally carloads of this whiting were consumed. It has now gotten back to Cape Cod. It makes a pretty good canned product and a nice paste. One-half percent of monosodium glutamate greatly improved whiting. Smoked oyster paste: 0.3 to 1.3%. Canned oysters: .1 to 2%. Canned fish cake: .2 to 3%. Canned crab meat: glutamate is not very satisfactory, but in canned products such as deviled crabs and crab pastes, it makes a wonderful improvement. Shrimp paste: a little but not too much gives zest to the characteristic flavor of the shrimp.

That brings me to a point that is new to most of us. I was in the Army working on foods in the Pacific during the war. One of the staples of the Jap soldier was canned fish products. They apparently will can any fish whatever. It was all very good, and for a long time we could not understand why. It was always packed with a sauce. What they were using was one of these hydrolyzed soybean products. They used this gravy in all of their canned fish products, and they also used it in their very low quality beef. In Japan the cow is used to cultivate the soil, and is killed for beef when she grows old. Naturally, this beef is tough. They canned that for their Army and added this same sauce; it was cooked under pressure to make it soft. It had an excellent flavor of the same sort as these fish products. By the way, our own men liked these fish products very much. They didn't mind the old canned cow too much either.

This product is very useful in marine products if added carefully. We don't want to kill the characteristic flavor of the sea foods. We must not destroy that flavor. We must add only enough monosodium glutamate to bring out that flavor, not so much that we cover it up.

What should you call it—is it flavor, seasoning, or salt? I think it is a seasoning, because it is a sort of an overall taste flavor and feel. It appeals to all of those senses. Therefore, I think it is different from salt, sugar or syrups of various kinds which we use in culinary work. I do think we ought to standardize the product. If we sell hydrolysates, let us sell them as such. The work we did was hit or miss. One thing

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flavor blend. If used in too low proportions one's money may be wasted since there will be no distinguishable effect on the taste buds of the consumer. On the other hand it appears that glutamate will stimulate taste only up to a point, beyond which additional increments are relatively indetectable. The optimum proportion must be determined experimentally but will probably lie between .1 and 1% of the total weight of the food as eaten.

Since the matter of flavor appears to depend on a total effect composed of many individual taste stimuli, the introduction of glutamate into a food specialty formulation will require a new study of the desirable proportions of other flavor modifiers, such as sugar and salt. In the presence of thickening agents such as gums, flour, and starches higher levels will be required than in unthickened products.

After one arrives at a good blend of glutamate with other flavor-bearing components, it is necessary to observe the changes in flavor which may develop during storage of the food specialty. The persistent quality of glutamate is retained indefinitely, regardless of storage conditions. Hence, it may increase in prominence with time as other flavors change or lose their strength. One must accordingly study the long range as well as the immediate effect of the quantity of glutamate used.

Monosodium glutamate is likely to be the most expensive seasoning added to the formula. Thus one must consider carefully the economics of its use. It seems unlikely that it could pay its way in a specialty costing ten or fifteen cents per pound, though it might prove well worth while in a food product costing fifty cents per pound. Another aspect of this evaluation is the necessity for using the isolated pure glutamic acid salt. In many products the mixed amino acids present in protein hydrolysates may be used satisfactorily, thus avoiding the cost involved in the separation and isolation of the glutamate. In any case, amino acids are expensive flavoring and nutritional materials and if used at all in food specialties they will need to be kept at a minimum level compatible with other requirements.

It is quite evident from the discussion which has been presented here today that there exists considerable difference of opinion as to the nature of the glutamate flavor. I am by no means sure that my remarks will clarify the situation at all. It is quite possible that the result will be "confusion worse confounded."

The approach which I shall make to the topic assigned me is one based on experience and observations over a period of several years in directing the development of food specialties. For the purpose of illustrating the considerations involved in such developmental work I shall discuss the various steps necessary in bringing out a food specialty.

When one has been given the assignment to work up a certain type of food specialty, one first takes into account the ingredients with which he has to work. We have the rather major items such as salt, sweetening agents, flour, and fats. Along with these we have seasonings, condiments, spices, flavoring agents, eggs, meat products, and a host of other possible ingredients. The first responsibility is the determination of the general characteristics of the food specialty desired and

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on the basis of these to select the major components. Since flavor appeal is the prime requisite of any food, the selection of ingredients must always be done with an eye to their effect on flavor. If we wish to consider glutamate as an enhancer of flavor in the food specialty under study, it is necessary to evaluate its compatability with the flavor of other major ingredients which are planned for use in the new food specialty. Glutamate has been found to be a good adjunct for meats, fish, chicken, eggs, soups and gravies. It is useful to give flavor to bland foods such as fresh vegetables. There are some foods with which glutamate does not blend well—such as cereals, fruits, canned vegetables, and dairy products generally. Glutamate usually is a flavor plus when combined with salt and sweet flavors. With sour and highly acid flavors it will probably not be compatible, particularly if the pH is low. In general, the greatest flavor value will be obtained from glutamate in foods with a pH range from 5.7 to 6.2. It is here that one gets the most value in the seasoning of food with glutamate.

In considering whether glutamate should be employed in our theoretical food specialty, we must remember that glutamate creates a persistent, lingering flavor reaction. For this reason it is not suitable in foods or drinks where it is important that the flavor vanish quickly. One would not use it in such a drink as Coca-Cola where a lingering flavor is undesirable. We will assume for the sake of the example that we have reached a decision that glutamate is compatible with the other major ingredients of our projected food specialty and that we find a lingering effect desirable in this product.

The next question to be decided is the level of use at which we should employ glutamate in the food specialty. The deciding factor here is the flavor of the product. Guided by our taste buds we can decide when we have reached the best formulation as regards glutamate. If an insufficient amount is used, one which does not produce a detectable difference in flavor, it is probably a waste of money. One should either use a sufficient quantity or not use glutamate at all. My own experience leads me to believe that one is apt to find the most useful level in the range of 0.1% to 1.0% of the total weight of finished product as served. The exact level can be determined best by the use of a taste panel. In our laboratories we use such panels a great deal in our formulation work. The people who constitute these panels are pretty well trained to distinguish flavors. The combined judgment of a group of individuals has proved a better guide in our developmental work than the opinion of a single expert in the field.

The flavor appeal of the finished food specialty is going to depend upon a blended effect resulting from the many taste stimuli furnished by the various ingredients. For this reason after we have tentatively

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settled on the optimum amount or minimum amount of glutamate to use with our other ingredients, it will probably become necessary to restudy the levels of the other components. We might need to reduce the salt or the sweetening agents because of the addition of the glutamate. We might find that there is some other marked flavor which is not compatible with the glutamate. So it is that one may need to do a complete reblending job in the light of the glutamate addition.

In such a study of reblending of ingredients one inevitably gets around to the problem of the cost of the ingredients. Economic considerations and potential market price are going to have a bearing on the quantities of certain components which we will be compelled to use. For example, if we need a certain viscosity in our product we might use a number of thickening agents. Expensive gum constituents might be effective in small quantities. Cheaper thickeners such as flour or starch may give the required viscosity, add a desirable bulkiness to the product and cost less money. On the other hand, their effect on flavor may be considerably less desirable than that of gum. In any case if we have settled on a level of glutamate before we have arrived at the proper viscosity, it will be necessary to go back and resurvey the blend of flavors and the amount of glutamate used. The reason for resurveying is that any of these thickening agents act as diluents of flavor and may selectively mask certain flavors more than others. In studying our blend of flavors it may now be thought that the addition of monosodium glutamate has made the product too sweet because, as has been described here today, glutamate has a certain sweet characteristic. If we need to take out some sugar because of this, we will be short in our package weight provided that there is a definite minimum weight which has been determined upon by reason of other considerations. This might suggest that we replace cane sugar in the formula with corn sugar and thus increase bulk without increasing the sweetness. On the other hand, because of the salty taste of glutamate, the level of salt originally used might prove to be too high. If the sauce or the soup or whatever specialty now proves too bland even after glutamate is added, we may need to increase the amount of glutamate to obtain the all-over stimulus or blended flavor we want. We might find it desirable to add onions or spice in order to sharpen the flavor of the specialty.

One point which may prove difficult from the standpoint of economy is that glutamate is an expensive ingredient for most food specialties. This consideration might well lead us to try mixed protein hydrolysates instead of purified glutamate. In many cases it should be possible through selection of the right hydrolysate to obtain compatible flavors at a lower cost per pound of amino acid flavor. Since the subject of

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the mixed protein hydrolysates is to be discussed by another speaker, I will not dwell on this point further.

In my estimation taste panels are very important in the formulation of these food spcialties. They enable one to measure the results of efforts to blend flavors in the formula of the specialty. The most satisfactory approach is to take only two or three samples at a time and ask the members of the panel to measure both difference and preference. Differences are particularly important because we need to make certain that the changes in formulation are detectable by taste. We feel that the preference of the trained testers is likewise valuable as a guide in formulation. But this is by no means a final yardstick by which to measure consumer acceptability for the specialty. That can only be evaluated through consumer taste testing when one has settled on an acceptable formulation. After one has exhausted the resources within his own group in testing and experimentation, he needs to seek a larger group. This can best be done through some agency or organization which specializes in this type of study. Thus one can reach a large group of people with the proposed food specialty and have it tested under normal home conditions. It is to be hoped that the directions will be followed carefully and that the results recorded from the various consumers can serve as a measure of the acceptability of the flavor of the product to the general public. I will not go into the techniques of getting and evaluating such answers, but I question the validity of the procedures generally used. Whether the results of such a consumer taste test can be viewed as a cross section of general national acceptance of the flavor is debatable.

At the time one has completed the formulation of what has become an acceptable food specialty and initiates consumer taste tests one should also undertake storage tests. The necessity of long-range thorough studies of the formulation of the proposd specialty under various storage conditions cannot be overemphasized. It is particularly important to observe the changes in flavor which occur during storage. Proper characterization of these changes may give an index to the causes of the same. One point to note particularly is the fading of other flavors since glutamate is persistent and might become too prominent after storage. The same thing is true of onions and spices. If certain flavors become too prominent during the storage tests, one will then need to go back and change the formulation of the specialty. Thus, it is only upon the completion of storage studies that one can feel that the formulation job is satisfactorily done.

One other change may occur during the storage tests which would prove detrimental to the new product. The so-called "browning reaction" between sweetening agents and glutamate might take place and lead to either undesirable flavor or undesirable color. Such a result

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would require that the old question of formulation be reopened, and conceivably it might cause the complete elimination of glutamate from the formula.

Finally, there is the question of the cost in using glutamate. It is apt to prove the most expensive component used in the food specialty. At its present price it is not likely that you will be able to use it justifiably if the selling price of the specialty is to be in the range of 15c to 20c per pound. On the other hand if the product can command a price of 50c per pound it might well prove profitable to use glutamate as an ingredient. In many cases I think it is probably necessary to use glutamate in the pure form. In other instances, however, the mixed hydrolysate may prove equally satisfactory and less expensive. For example, in bulk foods for relief feeding one might very well use a rather low-cost mixed protein hydrolysate. In conclusion, I would emphasize that one must always remember that at best the amino acids are expensive flavoring and nutrient materials and, if used, should be kept at a minimum level compatible with other requirements.

Protein Hydrolysates as a Source of Glutamate Flavors

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Author's abstract

The characteristics of a desirable protein hydrolysate to be used as a flavoring and seasoning agent include the presence of glutamic acid up to 16%, a large representation of individual amino acids, and a low fat and carbohydrate content. Wheat gluten, casein and soya flour are good sources for preparation of superior quality protein hydrolysates.

It is considered that a mixture of MSG and protein hydrolysate gives the most desirable results as to flavor and economy.

The flavoring of foods with protein hydrolysates has shown interesting and rapid progress in this country during the last decade. Since the production of protein hydrolysates, as such, has reached sizable quantities and their use in the food industry attained significant volume, specific information concerning their contribution to food flavor, and particularly regarding their source as glutamate flavors, should be more generally known.

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The purpose of the incorporation of protein hydrolysates in foods is to improve the flavor and taste of the products so as to make them more delicious. For more than 40 years, in China and Japan, it has been common practice to use protein hydrolysates from one source or another, as condiments. In the relatively short time that the American food industry has become interested in these flavors, outstanding improvements have been made in their manufacture as the result of chemical and nutritional research.

A rather voluminous literature has been developed on proteins and amino acids, and it has been exceedingly valuable in improving the manufacture of hydrolysates. A considerable number of patents have been issued, some under the title-subject "Protein Hydrolysates," and others designated "Flavoring Materials from Hydrolyzed Proteins." The numerous patents are evidence of the wide interest in these products.

Protein hydrolysates for foods consist essentially of two types: (1) complete acid-hydrolyzed proteins, and (2) acid-hydrolyzed proteins from which glutamic acid has been extracted. Both types are manufactured as liquids and commercially dry powders. This discussion is primarily concerned with the hydrolysates of Type 1, that is, the unextracted variety. It should also be stated that soya sauces and other flavoring meat sauces are produced wholly or partially by enzyme hydrolysis and that their production is of appreciable volume.

Protein hydrolysates made with sulphuric acid as the hydrolyzing agent have not been generally acceptable for food purposes, principally because of inferior or undesirable taste factors and their comparatively high cost of production.

Much has been written about meat flavor, but the subject remains far from clear. It is evident that meat flavor is due to something more than monosodium glutamate and that part of the flavor of meat is apparently due to nitrogen bases and slightly volatile organic acids. Recently, we have found that cooked fresh meat as well as cured meat contains small amounts of amino nitrogen. This indicates that meat flavor, to some extent, is tied up with amino acids. It is well known that monosodium glutamate contributes much to developing a good chicken flavor in soups and makes vegetarian food more appetizing. We also know that monosodium glutamate contributes not only to chicken flavor, but also to meat flavors in general.

Meat flavors have been discussed and advertised as amino acid flavors. This may not be entirely true, but certainly the amino acids which are present in meat protein definitely contribute to the flavor we all like in this important food. We have never had the opinion that monosodium glutamate, by itself, was entirely satisfactory for flavoring

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food products. Our experiments have indicated that hydrolysates which have a combination of all the amino acids seem to give a preferred quality rating, a more satisfying flavor and a more acceptable taste than when only one of the amino acids is present. The only possible exception to this opinion is with respect to the use of monosodium glutamate in chicken soups.

We believe the "non-essential" amino acids in most instances contribute better flavor than the "essential" amino acids. Certainly, we are agreed, from experimental evidence, that several of the amino acids and their derivatives, exclusive of monosodium glutamate, have flavor significance. For example, glycine, alanine, proline, leucine, serine, phenylalanine and aspartic acid have varying sweet tastes and contribute flavor. Methionine and cysteine impart definite desirable tastes and when heated provide strong pyrogenic flavors. Valine and tyrosine are slightly bitter. These observations refer to the dextrorotatory form of the amino acids. Since the four components of taste are described as sweet, sour, salty and bitter, it is clearly obvious that protein hydrolysate containing all or most of the amino acids has the constituents present to supply full and complete taste characteristics.

In this respect, we can liken protein hydrolysate flavors to a perfume which has been developed into a pleasing, attractive and thought-provoking bouquet by the blending of various aromatic essential oils, any one of which would not be attractive to "milady," but which when blended together, would give the appealing aroma which is so alluring. The same comparison can be made of the flavors derived from the presence and the blending of amino acid derivatives in a protein hydrolysate.

Investigations relative to the improvement of protein hydrolysates have developed definite fundamental information. The importance of the protein hydrolyzed cannot be emphasized too strongly. It has been proved that the protein should be high in total nitrogen, adequate in respect to all the amino acids, and should be specifically selected on the basis of the glutamic acid content so as to give the maximum of flavor. Commercially, these proteins are wheat gluten, corn gluten, extracted soya bean flour, casein, peanut flour, yeast, dried distiller's solubles, extracted cottonseed meal and fish waste. It is to be understood that there are also other proteins, such as egg albumin, that can be and which are sometimes used.

Frequently, a combination of proteins is used and in certain instances excellent tasting hydrolysates with superior qualities are produced, such as when wheat gluten, casein and an extracted soya flour, in proper proportions are hydrolyzed with hydrochloric acid. We know of one combination of these three proteins which produces an un-

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usually good, dry hydrolysate containing from 16 to 18 percent monosodium glutamate. This product has met with a ready reception from the food industry. Another combination of proteins is wheat gluten and casein which, in the correct proportions, give a hydrolysate with a high monosodium glutamate content and excellent flavor.

The protein used should contain only very small amounts, if any, of carbohydrates and fatty materials, since these constituents are frequently the source of unpalatable flavors. If the protein has appreciable quantities of carbohydrates and fatty substances, these materials should be substantially eliminated before hydrolysis.

Thus, the studies which have been applied to the utilization of protein-containing matter for the manufacturing of protein hydrolysates and amino acid flavors have shown that the type of protein and its ratio of amino acid content are fundamental concepts.

Table I gives the approximate glutamic acid content of several natural protein materials.

Table I

	Approximate Glutamic Acid Content of Proteins in percent
Wheat Gluten	36.0
Corn Gluten	24.5
Zein	36.0
Peanut Flour	19.5
Cottonseed Flour	17.6
Soya Bean Flour	21.0
Casein	22.0
Rice	24.1
Egg Albumin	16.0
Yeast	18.5

From this table it can be seen that one of the most acceptable protein materials is wheat gluten. Wheat gluten contains from 80 to 90 percent protein, is fairly adequate with respect to its amino acid content and is high in glutamic acid. Casein is also an excellent protein with good glutamic acid content. Soya bean flour and yeast are good proteins. Extracted edible cracklings are a fairly good protein, but not very high in glutamic acid content. The cost of the protein used

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for hydrolysis is also important, and the proteins named are reasonably priced. The Chinese and Japanese have used many kinds of fish and fish waste, but very little of this material has been utilized in this country, for several reasons, one of which is the difficulty, even by hydrolysis, to eliminate the undesirable fish odor which seems to carry over into the finished hydrolysate.

Raw protein material containing large amounts of carbohydrates often produces bitter tasting flavors. Fatty materials present during the hydrolytic process have an effect upon the taste and keeping qualities of the hydrolysate because of oxidation and rancidity development. Since hydrocholoric acid is usually the hydrolyzing agent for food hydrolysates, the sodium chloride content of the final product is appreciable as a result of neutralizing the excess acid with soda. Therefore, only enough acid to give a slight excess for hydrolysis is needed. The salt content in a good hydrolysate powder should be 35 to 40 percent, and in a good liquid hydrolysate 12 to 18 percent. However, a majority of the products now on the market in the dry form contain 45 to 55 percent salt and in the liquid form 20 to 25 percent. A study of Tables II and III will reveal the requirements of a good protein hydrolysate and the points at which some of those produced commercially are deficient.

Commercial production of satisfactory hydrolysates is also dependent upon other factors, such as the elimination of toxic metals and metallic contamination. This requires, among other things, first class corrosion-resistant equipment. Recent trace metal research has definitely indicated that trace amounts of metals can promote flavor abberation, deterioration and destruction of these products.

With respect to the drying of liquid hydrolysates, many variables—such as temperature, time, type of drying and cooling—must be considered. Temperature and time particularly are important to consider during the hydrolysis period, for too long a hydrolysis time and too high a temperature often result in objectionable unpalatable products. Likewise, fermentation, decolorization and neutralization of excess acid after hydrolysis are all important procedures to consider in the production of hydrolysates of acceptable quality. Probably one of the most difficult production factors is to produce a protein hydrolysate powder with only slight hygroscopic properties. However, there are several hydrolysates now being manufactured which are commercially available—excellent in flavor, with high monosodium glutamate content and which are only slightly hygroscopic under normal atmospheric conditions. The scientific use of proper proteins aids materially in lessening the hygroscopicity of the completed hydrolysate powder.

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Table II

Typical Analysis of a Good Protein Hydrolysate

Moisture	2.2%
Sodium Chloride	39.8%
Total Nitrogen	6.8%
Amino Nitrogen	4.7%
pH (10% solution)	5.2

Calculated Amino Acid Composition

Amino Acid	*As Is Basis Percentage*
Arginine	2.0
Histidine	1.0
Lysine	1.4
Tyrosine	1.7
Tryptophane	Trace
Phenylalanine	2.4
Cystine	0.5
Methionine	1.2
Threonine	1.3
Leucine	2.9
Isoleucine	1.7
Valine	1.8
Aspartic Acid	4.1
Glutamic Acid	12.0
Equivalent to Monosodium Glutamate	16.03

Control points to consider in selecting a good, commercially dry, protein hydrolysate are as follows:

1. Moisture should not exceed 5%
2. pH should be in the range of 4.8 to 5.4
3. Sugars should be absent
4. Taste should be neither scorched nor bitter
5. The product should be easily soluble in water
6. The salt content should not be more than 40%
7. The amino nitrogen should not be less than 4%
8. Monosodium glutamate content should not be less than 12%
9. The color should vary from light tan to caramel providing the other properties are satisfactory

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Table III
Analyses of Commercial Protein Hydrolysate Powders

Sample #	Sodium Chloride %	Amino Nitrogen %	Moisture %	MSG %
1	50.25	5.65	6.25	
2	47.04	3.60	16.88	
3	58.45	3.16	2.77	2.41
4	56.19	2.50	12.88	
5	47.79	4.88	4.77	11.40
6	76.57	1.68	3.62	
7	59.66	2.25	4.53	
8	65.76	1.97	5.11	
9	39.83	4.71	2.15	16.50
10	34.05	5.50	4.00	18.20

In comparing tastes with amino nitrogen content, the higher the amino nitrogen, the better the taste.

In evaluating protein hydrolysate for foods, there should be more specific standards than there have been in the past. This would promote and eventually bring about the manufacture of the best possible products of constant and comparable quality with an acceptable minimum monosodium glutamate content.

Numerous formulations of food products using a high quality protein hydrolysate in comparison with monosodium glutamate have been made. Frequently, dependent upon the type of the food product, its taste and appearance, tests have indicated the use of a protein hydrolysate. Products which have been investigated, among others, include bouillon, soya sauces, dehydrated soup mixes, gravy powder, sausage meat, processed meat, stews, corned beef hash, bakery products and many other foods as shown in Table IV.

Table IV
Uses for Protein Hydrolysates in Food Products

Soups	Headcheese	Bread
Stews	Mincemeat	Macaroni with meat sauce
Broths	Sausage meat	Poultry stuffing and basting
Bouillons	Curing compounds	Chow mein
Bouillon cubes	Goulash	Processed meat
Fish	Biscuits & crackers	Hash
Gravies	Fruit cake	Meat sauces
Scrapple	Spice mixtures	Hors d'oeuvre pastes
Sandwich spreads	Chop suey sauce	Cheese spreads
Pickle relishes	Cheese rarebits	Mayonnaise
Baked beans	Chili sauce	Dog foods
Pancake flour	Salad dressings	

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It is admitted that in chicken soups, both liquid and dehydrated and perhaps in other light colored soups, monosodium glutamate is the flavoring of choice not only because of taste factors, but because the Maillard reaction proceeds much more slowly, if at all. However, in chicken soup mixes, both liquid and dry, excellent results and stable color reactions have been observed when a 50 percent mixture of glutamate and a protein hydrolysate powder have been used, especially when sucrose replaces dextrose in the formulation—using only 60 percent as much sucrose as dextrose. The protein hydrolysate used in these experiments contained approximately 16 percent monosodium glutamate and was processed from a combination of wheat gluten and extracted soya flour. With hydrolysate products containing small amounts of monosodium glutamate, such as those produced from materials from which the glutamic acid had been commercially extracted, the results were exceedingly unsatisfactory with reference to taste, color and flavor acceptability.

In this discussion it is important to touch briefly on the economics of protein hydrolysates compared with monosodium glutamate. Tests have indicated that a comparison of monosodium glutamate and a good protein hydrolysate gives a respective flavor value in the ratio of approximately 1.25 to 2. On the basis of this ratio at 60c per pound for protein hydrolysate as against $1.50 for monosodium glutamate, the costs are respectively $1.20 and $1.87½, representing a saving of 67½c per pound when protein hydrolysate is the flavor. If these ingredients are used in sucrose-containing dehydrated chicken soup formulae on a 50-50 basis in the amount of 5%, the cost would be $5.25 per hundred pounds as against $7.50 per hundred pounds if monosodium glutamate only were used. This saving would be a very substantial one in the manufacturing cost of any product.

Further, on the basis of 60% flavoring amino acid salts in protein hydrolysates, the cost of flavor is $1.00 per pound of flavor compared with $1.50 per pound of flavor when monosodium glutamate is used. As has been mentioned, some hydrolysates are produced as a by-product from monosodium glutamate manufacture and in the dry form they contain from 3 to 5 percent of monosodium glutamate. These products are sold at prices within the range of 20 to 30 cents per pound. If they contain the apparent optimum of 5% monosodium glutamate and sell at the lower figure of 20c per pound on the monosodium glutamate content alone, their cost is 64c per pound as compared with a 60c per pound cost for the unextracted hydrolysate containing an average of 16% monosodium glutamate. Usually the unextracted hydrolysate has a better color, more delicious taste, and less hygroscopicity than the extracted hydrolysate.

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Proper discrimination in selecting protein hydrolysates, or, careful compounding of hydrolysates and monosodium glutamate not only gives superior taste acceptability and flavor to your finished product but contributes desirably to a more profitable cost structure. If you have not done so, for your own satisfaction, conduct flavor tests with a good protein hydrolysate, monosodium glutamate and combinations of them in various food products; undoubtedly you will be surprised at your findings. For, unquestionably, you will find it is possible to produce products with superior taste and flavor characteristics and that you will also be able to extend and expand your use of protein hydrolysates.

From this discussion we hope sufficient confirmatory evidence has been presented to permit your agreement that protein hydrolysates scientifically made from adequate glutamic acid containing proteins are a splendid and desirable source for monosodium glutamate in the flavoring of food products.

References: (15) (16) (26) (37) (54) (57) (72) (77)

Discussion

Dr. Melnick: What procedure do you use for removing carbohydrate prior to hydrolysis?

Dr. Hall: Most of the proteins we get have very little carbohydrate present, but it is removed by treating with .5% solution of hydrochloric acid.

The Relation of Glutamate to the Browning Reaction

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Author's abstract

Various carbohydrate materials found in foods, in particular the reducing sugars, yield brown substances when heated. In the neutral range of pH in which glutamate is always used, various nitrogenous substances, in particular amino acid materials such as glutamate, make the browning reaction take place faster and at a lower temperature. Thus mixtures of carbohydrates and nitrogenous substances naturally occurring in foods can take part in browning reaction under common conditions of processing and storage and these reactions can be the causes of both important good flavors and of serious bad flavors. Browning, despite its great general interest, will be discussed only briefly because it is not directly related to the main theme of this Symposium, which is glutamate as a flavoring

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agent. The flavors produced by the browning reaction, both good and bad, are different from the flavor of glutamate. And although glutamate itself has a flavor which is very different from the flavors of the other amino acids, it behaves in much the same way as many other amino acids in the browning reaction.

The first part of this paper will deal with the general character of the browning reaction, that is, with the substances involved in the reaction and with the results produced. The second part of the paper will deal with the factors which influence the browning reaction: 1) the character and the concentrations of the reacting substances, 2) the moisture content of the product, 3) pH, 4) the time and temperature of the reaction.

In general, it may be said that browning takes place to an enormously lesser extent in dilute solutions such as liquid soup than in concentrated or dehydrated products and that browning in dehydrated products can be enormously decreased by drying the products to very low moisture levels. Unfortunately, there is very little exact information available about the degree of browning in products to which glutamate is usually added and of the contribution of glutamate to browning in these products. In most natural products there is a considerable supply of both carbohydrate and nitrogenous materials which can take part in browning reactions and the addition of glutamate can only serve to accelerate the browning. In such cases, browning can be controlled not so much by elimination of glutamate as by control of the time-temperature relations of the moisture, and of other factors which influence browning generally.

The main subject of this Symposium is glutamate as a definite chemical substance—how glutamate is manufactured, what flavor it has by itself, what effects it has on the flavors of foods. Apart from acting as a definite chemical substance with its own specific properties, however, glutamate can react with carbohydrates in foods to give brown substances, which may have either highly desirable or highly undesirable flavors. This browning reaction will be discussed very briefly, without chemical detail, since it is only indirectly related to the main subject of the Symposium. The purpose of discussing browning at all in this Symposium on glutamate is to call the attention of users of glutamate to the fact that the addition of glutamate to a foodstuff may influence the flavor of the foodstuff in ways not intended, due to the reaction of glutamate with food constituents.

The flavor contributed to a food by glutamate itself can be detected by tasting the food immediately after the addition of glutamate. The flavor due to browning, in contrast, develops only with time and can be evaluated only after processing and storage. Furthermore, whereas the flavor of glutamate itself is not greatly influenced by processing and storage, the browning flavor is very much influenced by the time and temperature of both processing and storage. The flavor of glutamate blends with many other flavors when a food is tasted, but the contribution of glutamate, nevertheless, is a specific contribution of a single substance which, at a given pH, is not changed by the other substances present whose flavors blend with the glutamate flavor. How much

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browning flavor is developed and what kind of a browning flavor is developed, however, are very much influenced by the other non-glutamate substances present in a food. This is quite apart from any blending of the browning flavor with other flavors. The glutamate taste is given only by glutamate. Other amino acids have very different tastes. Many nitrogenous substances, other than glutamate, however, can take part in the browning reaction. In particular, other amino acids can react with carbohydrates in quite the same way as glutamate, and with the development of pretty much the same browning flavor, which is very different from the straight glutamate flavor.

To sum up, in discussing the browning reaction we are not dealing with the properties of a specific substance with a specific taste, like glutamate, but with a non-specific reaction which can take place in the absence of glutamate. And the end effects of the reaction—both the amount of flavor formed and the character of the flavor—depend on the time and temperature of the browning reaction, and on the nature and concentrations of all the numerous substances which can take part in the browning reaction.

In general, browning takes place whenever carbohydrate substances are sufficiently heated. The brown water-soluble substances found all have about the same spectrum and, in most cases, the same type of taste. If the heating goes on long enough, insoluble black substances are found.

This browning reaction of carbohydrates is responsible for many of the important good flavors of foods. The flavors of breakfast cereals, of the crust of bread, of beer, of molasses and maple syrup, to mention only a few, are, in large part, due to browning. On the other hand, browning can cause actual spoilage, particularly in concentrated and dried foods. Indeed, the worst cases of browning in concentrated foods never come to common attention because browning kills the very possibility of the commercial existence of the food. Thus, browning is a common problem in any large food company with varied products, and it was a spoilage problem of great military importance during the war, especially when dehydrated foods were stored for long periods at high temperatures in the Pacific area. As a result of the bad military experience, the Quartermaster Corps has sponsored an extensive program of research on browning, which recently has been concerned, in large measure, with a study of the basic chemistry of browning. One of the observations which has been made in connection with the Army research program, an observation which remains to be investigated further and confirmed, is that the products of browning may have toxic effects as well as bad flavor.

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What is called browning is not a single, well-defined reaction. It is a great hodge-podge of reactions. But when one deals with those practical cases in which browning is enhanced by glutamate, a great many of the browning reactions can be eliminated. First of all, some carbohydrates, like sugar and starch, brown only when heated to temperatures much higher than those used in food processing. At the food processing temperatures, browning is obtained only from those carbohydrates which are very reactive in the browning reaction—mainly reducing sugar, such as glucose and fructose and their breakdown products, and in a minor way, the breakdown products of pectin and a few other carbohydrates. Secondly, glutamate is used at a neutral pH, and at a neutral pH even the more reactive carbohydrates do not brown except in the presence of nitrogenous substances such as glutamate.

We shall now discuss the factors which, at food processing and storage temperatures and neutral pH, control the rate and extent of browning, and hence control the production of flavors which may either enhance the good flavor of glutamate or spoil the product.

First of all, browning is influenced by the composition of the product, by the kinds and the amounts of both the carbohydrate and nitrogenous substances present. How much extra browning is caused by the addition of glutamate to a complex product which already contains nitrogenous substances capable of promoting the browning reaction cannot be predicted, but must be determined by experience. Unfortunately, there is no published information known to me about the effects of glutamate on the browning of commercially produced foodstuffs. It is doubtful that much varied information exists, even in the notebooks of the food companies, since it is only recently that quantitative measurements of browning have been made, especially of browning after storage.

The amount of added reducing sugar can influence browning, if the product is not already rich enough in browning sugar before the addition of any more. When browning is enhanced by the addition of reducing sugar, it is advisable to add sucrose, which does not promote browning, instead of glucose, which does.

More controllable, usually, than the concentrations of reactive carbohydrates and nitrogenous substances is the water content of the product. Any reaction in solution in which two or more components take part is very sensitive to the concentrations of these components. In accordance with this general principle, if a solution containing the components of the browning reaction is diluted, the rate of browning drops off rapidly. If the solution is concentrated, the rate of browning increases rapidly until the moisture content of the concentrate is

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so low that the reaction is inhibited by lack of water. Normally, the rate of browning is at a maximum when the water content of the product is 10-15 percent. Thus, browning is not a serious problem in dilute soups. In dried, unsulfited fruits there is less browning when the moisture content is 25 percent than when it is 15 percent. If the moisture content of dried fruits can be raised to 35 percent by the use of a suitable technique for the promotion of mold growth, then browning is still further inhibited. In dehydrated foods, the major method of preventing spoilage due to browning is the drying of the food to 0.5-5% moisture, the higher moisture being permissible in the starchy foods. Of course, the product has to be packaged in a moisture-proof container, if the moisture content is to remain low. Much of the spoilage of Army dehydrated foods could have been avoided if the dehydrated foods had been dried to lower moistures.

Another factor which controls browning in a major way is the heating of the foodstuff during processing and storage. The degree of heating is determined both by the temperature to which the food is heated and by the time it is kept at that temperature. The exact effect of increasing the temperature varies greatly from system to system, but it is always great. Usually, the time and temperature of processing are fixed by the requirements of sterilization. It is often possible, however, to increase the rate of cooling. The well-known phenomenon of stack burn, which is partly due to browning, is observed when heated cans are stacked too compactly and cooling is therefore slowed.

Heating at ordinary or even extreme storage temperatures has no marked effects in a short time, but storage times can be very long, and some browning can take place in storage. Storage conditions, in general, are more controllable than processing conditions. One can be careful about warehouse conditions, avoid large stocks in hot countries and in hot seasons, and take precautions to avoid part of the product being stored for a very long time before being consumed. In sensitive or critical cases, the product can be stored at freezing temperatures or at temperatures in the region of 50-60°F.

A word of warning about accelerated storage tests at elevated temperatures. Raising the temperature from 85° to 120° F. not only increases the rate of reaction but changes the character of the reaction. Thus, one cannot predict the long time course of the reaction at 85° F. from short time experiments at 120° F. The high temperature storage test is better than no storage test at all, but any temperature above 85° F. is suspect, and it is always safest to verify results obtained at high temperatures by long time experiments at the temperature at which the product is stored in real life.

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Browning of products such as noodle soup paste containing glutamate (55) and dried eggs (8a) which are consumed at a neutral pH, can still be prevented by acid if solid alkali is also added to the product in a suitable way. The alkali is separate from the acidified browning reactants during storage, but neutralizes the acid when the product is dissolved.

Sulfite, which has been used as a food preservative since prehistoric times, is a very effective inhibitor of browning, and is used as an inhibitor of browning in dried fruits. Sulfite, is not used, however, in foods containing glutamate, although it might be used in some cases were it not for legal restrictions.

In summary, glutamate in addition to its well-known flavoring effects, can also enhance the browning reaction. Since the flavor produced by the browning may develop only with long storage, it is important to examine foods, especially concentrated and dehydrated foods, to which glutamate has been added, not only immediately after preparation but also after storage. If bad flavor due to browning develops during storage, then browning should be measured quantitatively, and the composition of the product and the storage conditions should be varied in the ways which have been described until any bad browning flavors are eliminated.

Discussion

Dr. Melnick: Dr. Anson has directed attention to a very important point for consideration when monosodium glutamate is employed for improving the taste qualities of food products. In adding monosodium glutamate to foods, a reactant in the undesirable browning reaction is introduced. As has been mentioned, amino acids couple readily with reducing carbohydrates to yield pigments which are responsible for discoloration of the product and for off-flavors. In addition, changes in the texture of food products may become apparent and the nutritional value of the product is frequently impaired. In heat-processing foods, hydrolysis of protein occurs to a negligible degree; hydrolysis of polysaccharides, such as starches, to yield reducing sugars, however, does occur to an appreciable extent. Thus in supplementing a heat-processed food with a free amino acid, a reactant that is normally present in very small amounts would be added in concentrations capable of increasing the browning reaction to a noticeable degree.

The Office of the Quartermaster General is now responsible for procuring low-cost food mixtures for feeding the civilian population in occupied areas. We have been aware that these products cannot exhibit, because of the cost limitations, a high degree of taste acceptance. Accordingly, it has been recommended that some consideration

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be given to adding low-cost amino acid preparations to the product capable of imparting a meat-like taste. This recommendation has been made with some reservations, since frequently products formulated with added protein hydrolysates exhibit improvement in taste when sampled immediately after manufacture but are unpalatable following holding tests. The brown discoloration of the product and fluorometric analyses of the test extracts have indicated that deterioration of the product is due in large part to the reaction between the free amino acids contributed by the protein hydrolysate and the reducing sugars naturally present. This has been confirmed by tests conducted on control samples without the added protein hydrolysate; these exhibited insignificant browning.

Mention was made by Dr. Anson of a study leading to a patent* for the inhibition of the browning reaction in dehydrated foods. It is well recognized among food processors that a reduction in the moisture content is very effective in minimizing the extent of the browning reaction. However, I would regard this merely as a stop-gap solution since the necessity for reducing the moisture content to the low levels desired increases processing costs, requires elaborate packaging, and is often associated with reduction in the utility of the product. By utility is meant ease of reconstituting the product prior to consumption. By coating the principal reactant in a dry product with a barrier material capable of physically isolating the material from the other reactants present, the extent of browning can be materially reduced. The barrier material should obviously be non-toxic, palatable, and easily removed on reconstituting the product. A more effective means for inhibiting the undesirable reaction involves reducing the pH of the food mixture to a point where coupling between the amino acids and reducing sugars fails. The practical application of this observation forms the basis of the patent.

In one of the test systems (a noodle soup mix) monosodium glutamate was present in relatively high concentrations as the principal flavoring agent. It was demonstrated that by reducing the pH of the mix to 4.5 or less, deteriorative changes were markedly reduced. However, in many food compositions, a pH value below 4.5 is associated with an unacceptable sour taste. By including in the mix a solid alkalinizing material in a potentially active form, but physically isolated from the other materials present, it is possible to inhibit the browning reaction during the storage of the dry mix without interfering with the palatability of the reconstituted soup. Thus in the case of the noodle soup mix it was found that by fractionating the monosodium glutamate into glutamic acid and disodium glutamate, adding the glutamic acid di-

*Melnick, D., Composition and method, U. S. Patent No. 2,426,634, Sept. 2, 1947.

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rectly to the other ingredients in the mix (which included glucose), coating the disodium glutamate granules with hydrogenated fat, no appreciable browning occurred during the shelf life of the product. On adding water to the mix and bringing the suspension to a boil, the hydrogenated fat melted, liberating the disodium glutamate for neutralization of the glutamic acid, with the result that the cooked product was indistinguishable from that formerly made using monosodium glutamate.

In other products where the participants of the browning reaction cannot be so easily isolated, the procedure required modification. Thus in a tomato soup mix it was found satisfactory to add citric acid to reduce the pH of the product to 4.5 or less and to add sodium bicarbonate as fat coated granules for restoring the pH to the desired level on reconstitution.

Difficulties were encountered with some products when it was found that certain spices, for example turmeric, were fat soluble and behaved as pH indicators. These were observed to diffuse through the fat barrier, and on coming in contact with the alkalinizing agent exhibited a color change which rendered the product visually unacceptable. As a result, certain modifications in the barrier material were required.

It would seem that the basic principle described—that is, having the product in an acid state during storage with the alkalinizing agent physically isolated by a barrier material that can be easily removed during reconstitution of the product—may be applied with favorable results to the stabilization of other dehydrated products such as soup mixes containing protein hydrolysates, dehydrated eggs, dehydrated milk products, and others. This method, however, does not seem readily applicable to the stabilization of liquid soups because of the difficulty of physically isolating the alkalinizing agent. However, in such products the moisture content is usually sufficiently great so that appreciable browning does not occur. Whether the addition of monosodium glutamate to such liquid soups, canned and stored for appreciable lengths of time, will be responsible for objectionable browning remains to be demonstrated. Nevertheless, the potential difficulties arising on adding monosodium glutamate should be borne in mind, consideration being given particularly to the keeping qualities of the supplemented product, since improvement in initial acceptability should not be attained at the risk of impairment in acceptability.

Dr. Lightbody: We have had a certain amount of experience with dehydrated eggs, and there appears to be no doubt that a browning reaction is a factor in deterioration of egg white and powdered eggs. The reaction in which protein is involved is a factor in palatability

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changes, primarily from the standpoint of texture rather than flavor. The salt water soluble fluorescence test has been used as a means of estimating off-flavor in eggs. There are several conditions of storage and treatment of the powder which lead to marked lack of correlation of fluorescence and development of the undesirable flavor. That a protein carbohydrate reaction product is responsible for the flavor changes is very doubtful. In whole powdered eggs there is evidence of another type of browning reaction in which the amino group derived from liquids plays a part. This type of browning also can be estimated by a modified fluorescence test. The correlation of the extent of browning with off-flavor, like the correlation of the salt water soluble fluorescence, may, however, be only incidental. Regardless of what the true relationship is of browning, the texture and flavor changes, it is true that the changes can be retarded by adjusting the pH downward and the shelf life notably extended. The nature of the changes inhibited by acidification cannot be more than guessed at at this time. If there is any glutamic acid present in whole egg powder, it is probably a product of microbiological action since the quantity of free amino acids in fresh eggs is very small.

Mr. Heyl: In addition to eggs and dried soup mixes, what other products are browned by monosodium glutamate?

Dr. Melnick: Liquid soups, I would suspect, should be considered as potential browners.

Mr. Heyl: Is the browning objectionable? Is it perceptible?

Dr. Melnick: Yes. . . .

Mr. Thompson: Dr. Hall brought out the salient points as far as the trace metal aspects are concerned, and, assuredly, we have the trace elements to worry about. Although we have done nothing to show the trace elements to be involved in something like monosodium glutamate browning or amino acid browning in general, we have shown that trace metals play a rather important part in browning and that metal protein complexes may well catalyze general browning. We have shown that copper may combine with proteins and that the resulting copper protein will react with substances containing an ethylene bond in a ring structure resulting in a product which possesses browning characteristics. Unfortunately, I don't think it will add much to this particular program, because the results to date indicate that amino acids *per se* do not enter into this reaction.

Mr. Heyl: You spoke of carbohydrates in this reaction. Are there any phospholipids?

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Dr. Anson: No, these are the chemical breakdowns, not the pathological.

Dr. Hall: We have found that when hydrolysates are not adjusted to the proper pH you do get a very definite and very quick browning. We adjust our hydrolysates to a pH of 5.2, because some preliminary experiments in which we adjusted to 6 or 6.5 showed that the hydrolysate adjusted to 5.2 gave us less discoloration. Perhaps browning in some of the food products occurs because there is a break-off of the NO and NH_3 groups in the presence of free ammonia or because you have a break-off of the NH_2 group which reacted similarly to ammonia. In the manufacture of hydrolysates, a certain amount of ammonia is always given off. In this respect I believe you will find that you get less browning than when you avoid that. Acid must be a necessary adjunct to stopping or inhibiting the browning reaction.

The Significance of Thresholds of Taste Acuity in Seasoning with Glutamate

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Author's abstract

The definition of threshold is that intensity of stimulus which has a probability of 0.5 of eliciting a response. The presence of flavoring materials in foods at concentrations below their threshold levels has important effects on the appreciation of detectable flavors that are present in higher concentrations. Monosodium glutamate is an example of a substance which is used in some cases in subthreshold concentrations and yet has an effect on the flavor of the food. Some examples have been reported of enhancement of one pure taste by another but different workers are not in agreement as to which primary taste affects another.

It is possible that disagreement in results on enhancement and on the synthesis of complex flavors from primary flavors is due to a difference in taste thresholds of the judges involved. Reliable data must be obtained on the thresholds of acuity of the judges used in such tests and the comparisons made by individuals having similar threshold levels.

With the use of monosodium glutamate, the evaluation of food flavor is more elusive than with those seasonings which are added in such amounts that their quality may be identified as a recognizable component of flavor. From today's discussion it is apparent that the highly purified commercial product, the sodium salt of L (+) glutamic acid, has no odor and does not possess a meaty flavor. The protein hydrolysates have these qualities and do add a distinctive taste of their own

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to foods with which they are mixed. But not only is the flavor of monosodium glutamate elusive and delicate but in many foods it is used in relatively small quantities. So small, in some cases, indeed, that the effect sought is adjuvant rather than additive. That is, monosodium glutamate itself is not tasted, its effect on flavor depends on its modifying influence on flavors already present before its addition. This means, then, that monosodium glutamate often is used in sub-threshold quantities as a seasoning agent.

What is meant by a sub-threshold amount? This is a quantity which is below the minimum amount which can be recognized as a sensation—of taste, in this instance. Ideally, sensations, including that of taste, occur each as a continuum, a series of closely graded steps differing only in magnitude. There are two extremes on the taste continuum; at one end where concentration of the sapid substance is lowest, there will be no sensation of taste; at the other extreme, the concentration of sapid material will be so strong as either to disrupt the taste mechanism or to go beyond the limits of its sensory capacity and again no taste will be appreciated. There is an interval within these two extremes, nearer the lower end of the concentration range, where intensity of taste response gradually shades from none to a definite recognition of taste which always occurs. There is no single concentration above which a taste will always be experienced and below which a response never occurs. Such a quantity would be called the threshold concentration for that substance. However, due to the gradual tapering off of sensory acuity, an arbitrary definition of threshold has to be adopted. This is defined as that value of the stimulus—here the concentration of sapid substance—to which a response of taste occurs exactly half the time. This is the strength of stimulus which has a probability of 0.5 of producing a response. Persons differ widely in their stimulus threshold for bitter and there is a less degree of variation for sour, sweet and salty. Thus, no hard and fast assertion can be made as to exact threshold values—only a range for a population and a mean can be determined. Our results indicate that the threshold for monosodium glutamate is close to but somewhat below 0.0632%. Our work was done on the purified salt. A recently reported figure from another laboratory is approximately 0.0588%, also on a highly purified and odorless material.

Some preliminary work on attitudes toward various concentration levels of glutamate indicate a preponderance of unfavorable response above the threshold value. For pure taste modalities, the usual feeling tone is neutral, pleasant, neutral, unpleasant in order of increasing concentrations.

The fact that monosodium glutamate is a mixture of tastes may be

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responsible for its apparent non-conformity to the above characteristics.

Attempts have been made to synthesize the glutamate flavor, using pure solutions, each having one of the four recognized primary tastes. One proposed mixture consists of the following:

Sweetness (sucrose) at 0.6 threshold concentration
Sourness (tartaric acid) at 0.3 threshold concentration
Salty (sodium chloride) at 0.7 threshold concentration
Bitter (caffeine) at 0.9 threshold concentration (16)

The values for threshold concentrations were taken from the literature. An attempt to reproduce this experiment with ten subjects from the Food Acceptance Branch met with complete failure. Evidently the taste sensitivity of members of our group are different from that of the experimenters whose work we attempted to duplicate. Pursuing the experiment further, the concentrations of all components were increased to the threshold level and additional salt was added to 1.2 times the threshold for this substance. In one subject, this mixture did somewhat simulate the glutamate taste. Thus it may be that the sensitivity of the individual, as measured by his threshold values, determines his identification of a complex flavor.

Experimentation with several subjects whose thresholds were determined for the primary tastes would establish this concept or would indicate that complex tastes depend on integrative phenomena in the central nervous system beyond the additive effects of individual components.

Enhancement of flavor in mixtures is another aspect of taste physiology which has possible direct bearing on uses of monosodium glutamate. According to previous reports, sweetness increases the apparent intensity of the sour taste, due to a depression of the threshold for sour (60).

Other enhancement effects reported are slight with pure solutions of primary tastes. Other workers contradict the findings on sucrose, stating that sucrose has no effect on the sour taste (57). Thus, the field is largely an uncultivated one. A carefully planned series of threshold determinations, using mixtures of two substances at a time, one kept constant, and the other presented in a graded series of concentrations for threshold assessment, would throw light on a situation still in confusion at the theoretical level. Having mapped out accurate and reliable enhancement effects for the primary tastes, monosodium glutamate could be substituted and its effect on thresholds of salt, sweet, sour and bitter could then be accurately measured. From these data, a more reliable prediction of modifications of flavor by monosodium glutamate could then be made.

References: (16) (57) (60).

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Pharmacology of Glutamic Acid

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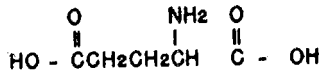
Author's abstract

Glutamic acid occurs naturally in large amounts in all complete proteins. It is non-toxic after single doses except when given intravenously, which produces vomiting in doses above 175 mg./kg. L-glutamic acid is more completely used by tissues while a high percentage of D-glutamic acid is excreted in the urine as pyrrolidone carboxyline acid. Glutamic acid does not raise the threshold to electrically or metrazol-induced convulsions. It does increase the I.Q. and produces beneficial effects in the behavior of mentally retarded children. Glutamic acid is an important constituent in many biologically active compounds such as Glutathione, Tyrocidine, Pteroyl-glutamic (Folic) Acid, Insulin, Tumor Tissue, "Diopterin," "Triopterin." An effective blocking compound of glutamic acid might be effective against cancer.

Glutamic acid was first isolated and identified as a natural body constituent in 1866 by Ritthausen (31) and synthesized by Wolff in 1890. It is the most abundant amino acid present in casein (63) and is a well-represented constituent of all complete proteins.

The molecular structure of glutamic acid is as follows:



The glutamic acid content of various proteins (31) is shown to be:

1) Gelatin 12.0%
2) Ovalbumen 13.3%
3) Ox muscle.....13.4%
4) Fish muscle.....13.7%
5) Glycinin 18.5%
6) Arachin 19.5%
7) Casein 22.0%
8) Glutenin 25.7%
9) Wheat gliadin.....43.0%

In a broad sense glutamic acid may be an essential amino acid for man (that is, essential for body growth, not essential for maintenance of body weight, but essential for other biochemical reactions). Other

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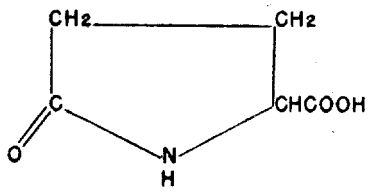
species, such as the dog and the rat, can readily synthesize glutamic acid (5). Both glycine and glutamic acid are required for optimal growth of the chick. Most textbooks state that D-glutamic acid is the naturally occurring optical isomer, but recent studies (61) indicate that L-glutamic acid is more completely and specifically utilized in the body while D-glutamic acid, when given in large doses, is excreted in the urine to a greater extent. In rats D-glutamic acid is converted to D-pyrrolidone carboxylic acid and excreted in the urine to the extent of 73% of the ingested dose (67). L-glutamic acid in this species is utilized more fully and excretion is evidenced by an increase in urinary urea nitrogen. D-pyrrolidone carboxylic acid has the following molecular structure:



Obviously the labeling of either isomer as the single naturally occurring chemical compound may be erroneous, since both occur in the body and if glutamic acid in isomeric form follows the rules of other optically active substances, the body will racemize the isomers so that the results must always be relative rather than absolute.

Glutamic acid has a rather marked specific dynamic action, being exceeded in this regard only by phenylalanine and tyrosine (8). It is also one of the amino acids which can form glucose or glycogen in the body (8). According to Channon, Mills, and Platt (11), of fourteen pure amino acids tested only glutamic acid, tryptophane, and tyrosine had any lipotropic activity.

In an attempt to determine the LD-50 of glutamic acid, large doses have been given both orally and parenterally to guinea pigs and mice in the author's laboratory. Compared to other substances glutamic acid is very non-toxic, since over 2.0 gm./kgm. fail to produce symptoms of toxicity in these rodents. When higher species are studied, we find that both glutamic and aspartic acid have a specific, toxic effect—that of producing emesis. This effect has been studied rather extensively in both dog and man since it represents one of the persistent toxic side actions of parenteral amino acid therapy. In other words, nausea and vomiting occur if protein digests are infused too rapidly intravenously. The following data from several investigators (51), (85), (69) indicate that aspartic acid is slightly more effective in producing this side

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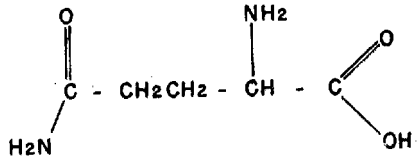
action than is glutamic acid, and that this toxic action can be prevented in the dog by small doses of either barbiturates or epinephrine.

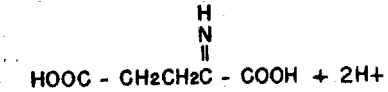
Investigator	Emetic Dose Glutamic Acid	Aspartic Acid
Madden et al (51)	100 mg/kg	—
Unna and Howe (85)	219 mg/kg	197 mg/kg (3 mg/min)
Roth et al (69)	136 mg/kg	— (10 mg/min)
Roth et al (69)	241 mg/kg + 2 mg/kg pentobarbital	
Roth et al (69)	198 mg/kg + 2 mg/kg epinephrine	

Unna and Howe found no essential difference between L-glutamic acid and the racemic mixture insofar as the emetic dose was concerned. The desaminated forms, glutaric and succinic acid, were much less toxic in this regard. Combining glycine with glutamic acid was not an antidote for the emetic effect.

If we now consider the unique utilizations of glutamic acid by the body, we find several interesting facts. Krebs (44) has shown (1935) that L-glutamic acid amide can readily be formed as an endothermic reaction in brain slices which may result in the absorption of as much as 0.8 percent of NH_3 per hour (dry weight). This unusual utilization of a single amino acid by cerebral tissue has been confirmed by Weil-Malherbe (87). The reaction product is called glutamine and may be used by brain tissue as a source of energy. The reaction takes place in the grey matter and retina of all species, and in the kidney of a few species. Glutamine is represented as follows:



Aqueous extracts from the tissues which synthesize glutamine contain a specific enzyme, glutaminase, which splits glutamine to glutamic acid and NH_3. Haber and Saidel (26) have recently found the free glutamic acid in rats' brain to be 125 mgm. percent while the total non-protein glutamic acid was 220 mgm. percent. During strychnine convulsions a decrease of 30 percent was found in the total non-protein glutamic acid. Krebs and Cohen (46) have also shown that glutamic acid may act as a hydrogen donor through its ketimine form as can be seen in the following:



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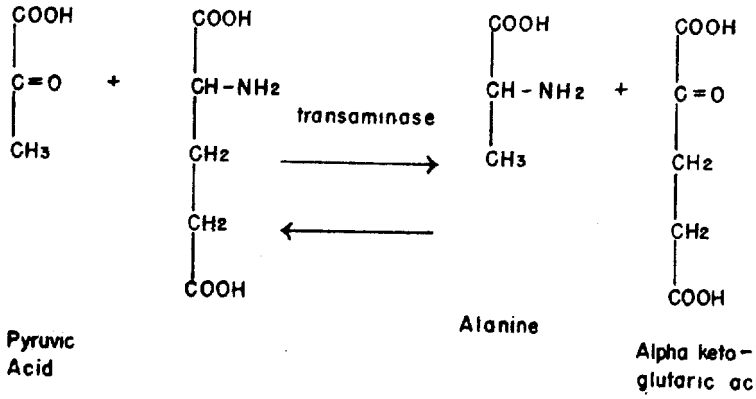
Glutamic acid may also be converted to alpha ketoglutaric by the enzyme transaminase (32), as is shown below:



The first clinical use of glutamic acid for its effect on the CNS was probably that of Price, Waelsch and Putnam (64) who in 1943 fed DL-glutamic acid (4.0 Grams T.I.D.) to epileptics in an attempt to utilize the acidifying effect of D-glutamic acid. The urinary pH was significantly lowered and in their opinion the petit mal and psychomotor types of seizures were benefited. Since the introduction of more effective drugs against petit mal, the anti-epileptic effect of glutamic acid is now considered insignificant by most specialists in this field, and it has been found to be completely ineffective as an anticonvulsant in laboratory animals (24). These pioneer workers did note, however, and reported, an increase in physical and mental alertness in the patients, which aided materially in their social and economic rehabilitation.

"Usually the patient is noted to be more energetic and happier, mood swings are less pronounced, behavior mannerisms are ameliorated and he is more congenial with associates."

This observation has been confirmed in trained rats by Zimmerman and Ross (95) and Albert and Warden (3). With an increase of glutamic acid in their diets, rats are significantly more capable in running a maze and in solving maze problems.

Groups of investigators headed by both Zimmerman and Waelsch have extended their studies to mentally-retarded children. Zimmerman and his colleagues (94) studied sixty-nine children ranging in age from 16 months to 17½ years. Before administering the glutamic acid the I.Q.'s were estimated. Six months later an average increase of seven had occurred in the I.Q. scores. All had gained in mental age—one as much as 16 months. Some retarded subjects showed remarkable improvement. A girl of nine years progressed in I.Q. from 69 to 87 and

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showed increased learning ability. A boy of sixteen learned to care for himself as his I.Q. rose from 50 to 60 in six months' time. Greater improvement occurred in tests requiring abstract thought than on those involving motor skill. Basic improvements in personality were also observed. The side effects of the therapy consisted of occasional gastrointestinal irritation, restlessness, overactivity and insomnia.

Albert, Hoch, and Waelsch (2) reported at about the same time on the effect of glutamic acid in 8 mentally deficient patients ranging in age from 6 to 26 years, but whose mental age ranged from 2 to 8 years. I.Q.'s varied between 22 and 73. The subjects were alternately given 9.0 grams of glutamic acid per day or placebo tablets. A significant rise in I.Q. was noted with the amino acid therapy. This improvement regressed during the period of placebo administration. These studies are now being extended to larger feeble-minded populations.

Considering our test methods one must be exceedingly cautious in interpreting the effect of glutamic acid on mood and intellectual performance. Unfortunately I.Q. tests as scientific methods are still somewhat in the category of the method used for weighing hogs in Arkansas. I am told that a plank is placed across a log with a box on either end. The hog is placed in one box and stones are placed in the other until balance is achieved. The weighers then stand around and guess how much the stones weigh!

Before a general program of glutamic acid therapy can be introduced for mentally deficient individuals or the public at large, the answers to the following questions should be known:

1) Is the increase in I.Q. real or due to better application and cooperation during the test?
2) Are subjects with normal intelligence benefited by glutamic acid therapy?
3) Will nervous disorders be increased as indicated by the side actions of restlessness and insomnia?
4) What is the effect of large and continued daily dosage of glutamic acid on longevity?
5) Is the glutamate effect modified by the other amino acids in casein? (The recent work of Christensen et al (13) indicates that when individual amino acids are fed, they compete with each other for concentration into body cells from body fluids.)
6) Are cancerous growths or cell rests matured by glutamic acid?

At present it is evident that this natural type of CNS stimulation is far superior and less dangerous than that produced by the foreign sympathetic amines such as benzedrine and desoxyephedrine. Considering the dosage used in food flavoring this level could only be beneficial.

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Potent agents containing glutamic acid:

1. Insulin 17.5% (G)
2. Tyrocydine (D-glutamic)
3. Glutathione
4. Pteroyl glutamic (folic) acid
5. Tumor tissue D? form
6. "Diopterin"
7. "Triopterin"

Since Kogl in 1939 (43) reported that D-glutamic was the type found in tumor tissue, a tempest in a teapot has raged over this broad generalization. Apparently to some biochemists, tumors are tumors. Their findings of glutamic acid content should be as constant as that found in the gray matter of the cortex. If cancer were that constant, the pathologist would not have to spend long hours deciding on the degree of malignancy, etc. However, the concept of D-glutamic acid in cancer has led to the synthesis and testing of two glutamate conjugates in experimental cancer. These drugs, "Diopterin" and "Triopterin," must be given parenterally since oral administration results in breaking the polypeptide linkages. Given parenterally, however, these drugs inhibit spontaneous mammary tumors in mice. In man, these drugs produce some regresssion of the tumor and have a definite analgesic effect against the pain of cancer. It is too early to determine how effective this therapy may be but it is an interesting lead. Specific blocking compounds of D-glutamic acid should be synthesized and studied to supplement these initial observations.

We have recently become interested in the derivatives of glutamic acid and arginine as the possible metabolites which might be blocked by the potent analgesic drugs. Since some of these compounds lower the normal pain threshold, we are desirous of obtaining all possible derivatives of these amino acids.

References: (2) (3) (5) (8) (11) (13) (24) (26) (31) (32) (40) (43) (44) (46) (51) (61) (63) (64) (69) (67) (85) (87) (94) (95).

Discussion

QUESTION FROM THE FLOOR: Is monosodium glutamate ever used in place of glutamic acid?

Dr. Pfeiffer: Certain groups have attempted to cut down the gastro intestinal irritation by neutralizing the acid, and the main reason for using glutamic acid is that it is available from most chemical suppliers. One could use monosodium glutamate as well.

Dr. Melnick: Didn't Zimmerman and Waelsch, also, demonstrate that on cessation of glutamic acid dosage, the I.Q. returned to that prior to administration of the amino acid?

Dr. Pfeiffer: Yes.

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Bibliography of Monosodium Glutamate and Related Literature

(Prepared by Dr. Donald Washburn)

This bibliography includes not only the references cited in the papers of this symposium, but also references that are considered pertinent and contributory to the subject of monosodium glutamate by the authors of these papers and other interested people. Among them, for example, are references on the determination of glutamic acid: (71) (72) (73) (84); dehydrogenase: (48); and glutamic acid as a component in a new growth factor, strepogenin: (70) (80) (89) (90) (91) (92). The extensive bibliography of Olcott and Brother (59) provides numerous additional references.

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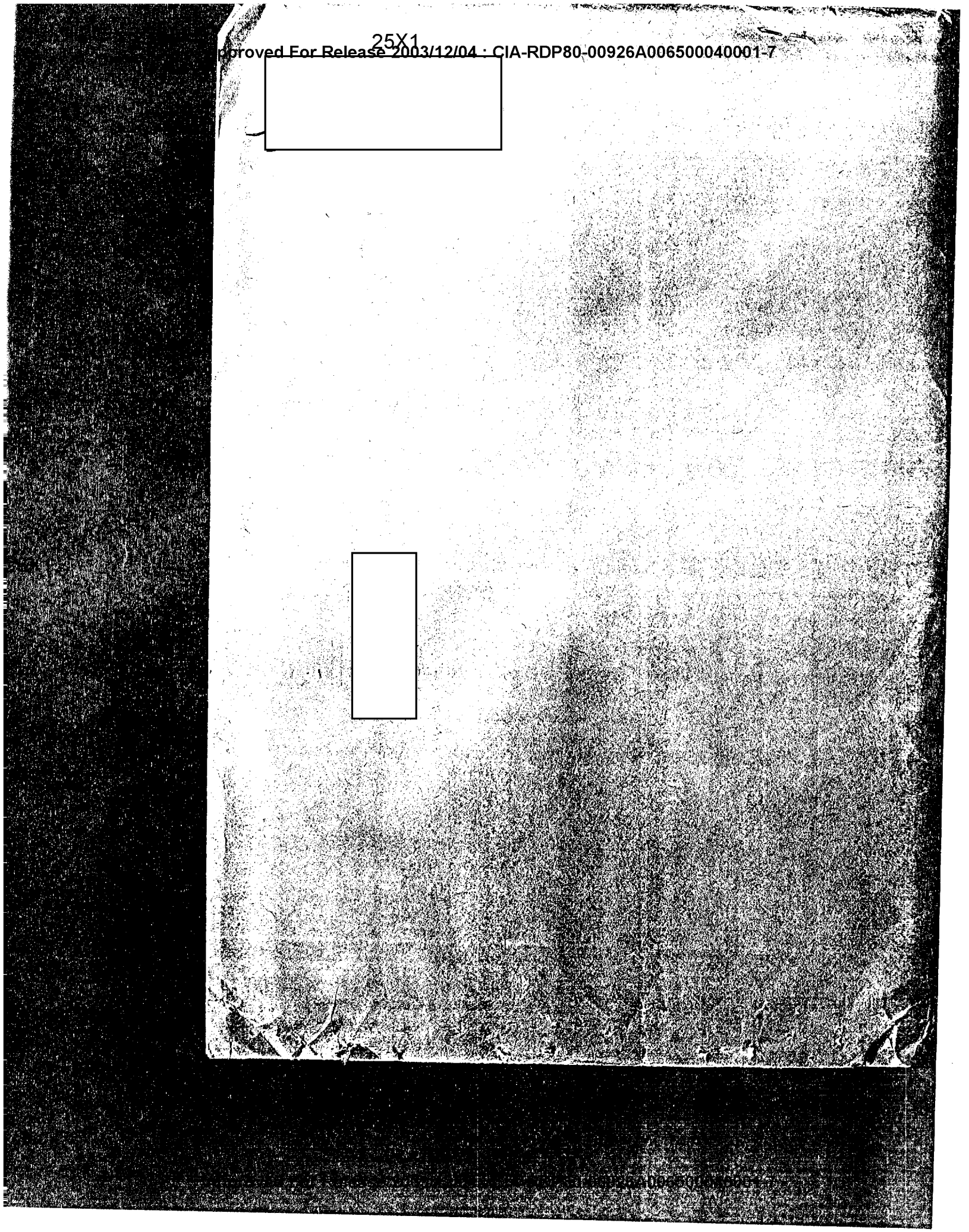

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