arabinose and D-galactose, a uronic acid pattern comparable to that of authentic glucuronic acid. Starch could not be found in any tangible amount in the polysaccharides.

Many of the polysaccharide materials isolated from the tomato pulp were strongly lyophilic. Substances having such properties and occurring in such quantities must contribute to the consistency or to the "body" of products prepared from the tomato.

Every 100 grams of tomato solids contain 60 grams of reducing sugars and about 3 grams of protein. These substances may produce off-color and undesirable flavor as a result of the browning reaction (*5*, *6*) and, therefore, may be regarded as sources of trouble in the preparation of tomato concentrates.

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FLAVOR EFFECTS

Possible Relationship Between the Ionic Species Of Glutamate and Flavor

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The unique flavor effect obtained when monosodium glutamate is added to foods has led to its wide use in the food industry. The fact that the effect is most pronounced between pH 5.0 and 6.5 suggests that only one of the ionic species of glutamate may be responsible for its flavor properties. A study of the equilibrium of the ionic forms of glutamate as a function of pH has shown that one ionic form of glutamate is predominantly present in the pH range 4.5 to 7.0. Comparison between the calculated percentage of glutamate present in this ionic form and the intensity of the glutamate flavor is in good agreement with experimental data from the literature. The ionic theory explains the noneffectiveness of glutamate in acid foods as due to the low equilibrium concentrations of the flavor-active ionic form at pH values below 4.0. A method is presented for estimating total glutamate concentration for desired flavor effect above this lower pH limit.

TO THE MONOSODIUM SALT OF GLUTAMIC ACID is attributed a unique characteristic known as a "glutamic effect" or "glutability." This effect is manifested by a marked persistency of taste sensation, a stimulation of taste receptors, and what has been described as a "tingling feeling" or a "feeling of satisfaction" (*3*). This flavor-enhancing property has led to wide use of monosodium glutamate in the food industry, but it does not appear to be universally applicable to all foods—for example, fruits, fruit juices, sweet baked goods, some dairy products and cooked cereals, and some products containing relatively large percentages of fat. The most useful level seems to lie between 0.1 and 1% and generally between 0.1 and 0.3% of the total weight of the finished product (*5*).

The foods in which the flavor effect seems greatest appear to lie in the pH range of about 5.0 to 6.5. This so-called "pH effect" has led to the speculation that only one of the ionic forms of

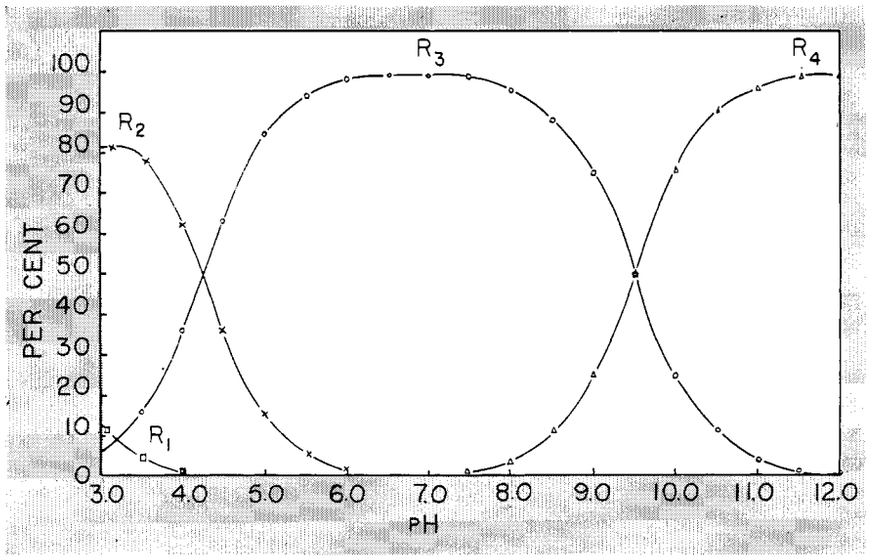
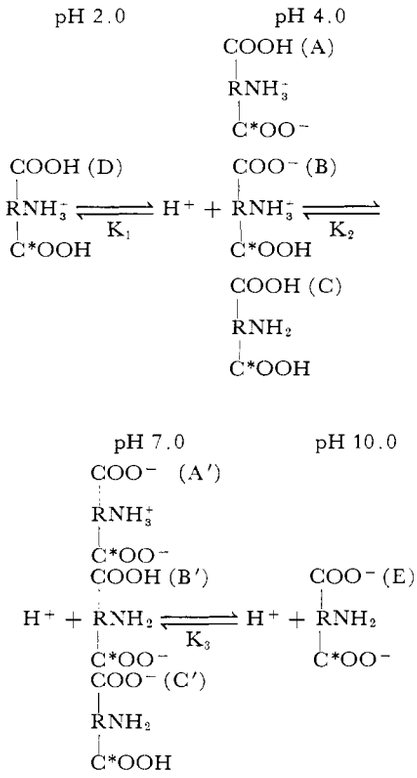


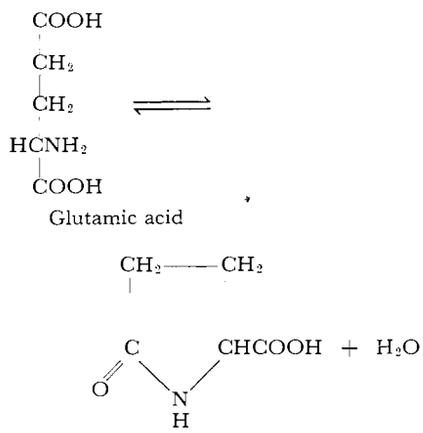
Figure 1. Percentage distribution of various forms of glutamate as dipolar ions as a function of pH

glutamate may be responsible for the unique flavor effects. Glutamic acid, an ampholyte, in solution is in equilibrium with a number of ionic forms, the distribution of which is governed by the pH of the solution. The dissociation of a dicarboxylic amino acid such as glutamic acid is described by Cohn and Edsall (*2*) and shown below:



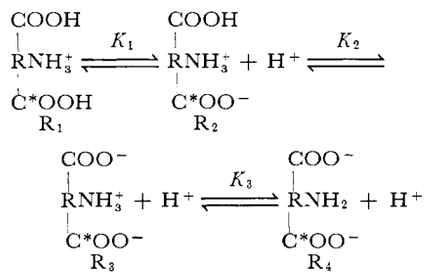
where R for glutamic acid is —CH_2—CH— and * indicates the α-carbon atom.

Under suitable conditions of heat and pH there is an equilibrium between glutamic acid and its lactam (pyrrolidone carboxylic acid).



Wilson and Cannan (*6*), who studied the glutamic acid–pyrrolidone carboxylic acid system, state that the lactam is in further equilibrium with its anion and the uncharged form. The present discussion considers only the system represented by Cohn and Edsall.

According to Cohn and Edsall, it may be assumed that only the ionic forms designated as D, A, A′, and E significantly contribute to the ionic equilibrium, so that their equilibrium may be rewritten as:



Thus, if glutamic acid or its soluble salts are dissolved in an aqueous solution, buffered to a given pH value, they will equilibrate into the various forms shown above. The distribution between the forms—i.e., the amount present in each form—will be determined largely by the concentration of hydrogen ion present in the solution. If the hydrogen ion concentration is known, the distribution can be calculated with the aid of the dissociation constants, K_1, K_2, and K_3. Cleaves (*1*) has presented formulations for such calculations:

$$(R_1) + (R_2) = \frac{(C)(H^-)^3 + K_1(H^+)^2}{(H^+)^3 + K_1(H^+)^2 + K_1K_2(H^-) + K_1K_2K_3}$$

$$(R_3) = \frac{(C)(H^+)K_1K_2}{(H^-)^3 + K_1(H^+)^2 + K_1K_2(H^-) + K_1K_2K_3}$$

$$(R_4) = \frac{(C)K_1K_2K_3}{(H^+)^3 + K_1(H^-)^2 + K_1K_2(H^-) + K_1K_2K_3}$$

where (R_1), (R_2), (R_3), and (R_4) represent the concentrations of the various ionic forms in mols per liter, (C) represents the total concentration of glutamate in moles per liter, and (H^+) represents the hydrogen ion concentration. If a total glutamate concentration of $0.01M$ is taken, which corresponds approximately to a 0.15% solution, and the values of 6.46×10^{-3}, 5.62×10^{-5}, and 3.16×10^{-10}, respectively, from Cohn and Edsall are taken for dissociation constants K_1, K_2, and K_3 at 25° C., the concentration of the several ionic species may be calculated at various pH values. These are listed in Table I and presented graphically in Figure 1.

Table I. Distribution of Ionic Forms of Glutamate as a Function of pH of Solution

	Percentage of Glutamate			
pH	R_1	R_2	R_3	R_4
12.0	...	...	0.3	99.7
11.0	...	...	3.1	96.9
10.0	...	...	24.6	75.4
9.0	...	...	76.0	24.0
8.0	...	...	96.9	3.1
7.0	...	...	99.8	...
6.0	...	1.8	98.2	...
5.5	...	5.3	94.7	...
5.0	...	15.1	84.9	...
4.5	...	36.0	64.0	...
4.0	0.9	63.1	36.0	...
3.5	4.0	80.9	15.1	...
3.0	13.4	81.3	5.3	...

Most foodstuffs are well buffered, so that glutamate added to a 0.15% level will not appreciably affect the pH of the system.

Reference to Figure 1 indicates that glutamate in the form designated as R_3 is predominantly present in the range pH 4.5 to 7.0. It seems to be well established that glutamate is most effective at pH values from about 5.5 to 8.0 (*4*, *5*). In

this pH range, glutamate is about 94% in the R_3 form at pH 5.5, close to 100% at pH 7, and about 97% at pH 8 (Figure 1). Further support to the theory that the R_3 form, $-OOC-R-COO^-$, may be
NH_3^+
largely responsible for "glutability" is furnished by Galvin (*4*), who reported that solutions containing 0.5% glutamate and 1% salt, and adjusted to pH values from 3.3 to 8.0 all had essentially the same taste at pH 6, 7, and 8. At pH 5.0, the normal glutamate taste was noticeably reduced to approximately 80% of the original intensity. Figure 1 indicates that 85% of the glutamate is present in the R_3 form, which is in good agreement. Galvin stated that normal glutamate taste was further reduced with a decrease in pH, which is also in agreement with the theory.

If the R_3 form is responsible for "glutability," then in order to obtain the same flavor level at pH 5.0 as at 6.0, more total glutamate would be required—that is, 1.00/0.85 or 1.17 times as much glutamate would be necessary to obtain the same concentration of the R_3 form at pH 5.0 as at pH 6.0. Similarly, at pH 4.5, 1.0/0.64 or 1.56 as much glutamate would be required to obtain the same concentration of R_3 as at pH 6.0.

There appears to be a lower limit of pH (about 4.0) below which it would become impracticable to add glutamate, because of the rapidly decreasing equilibrium concentrations of the R_3 form.

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HERBICIDE RESIDUES

Determination of 3-(*p*-Chlorophenyl)-1,1-dimethylurea In Soils and Plant Tissue

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The use of 3-(*p*-chlorophenyl)-1,1-dimethylurea as a herbicide required the development of a simple, accurate method for detecting and determining residues in treated soils and plant tissues. The sample being analyzed is disintegrated by digestion in strong alkali, and the 3-(*p*-chlorophenyl)-1,1-dimethylurea is quantitatively hydrolyzed to *p*-chloroaniline. The resulting aromatic amine is automatically removed and concentrated into a minimum volume of organic solvent. It is then extracted with dilute acid and determined colorimetrically. The method is applicable for determining microgram quantities of 3-(*p*-chlorophenyl)-1,1-dimethylurea in all types of soils examined and in a wide variety of crops The procedures are capable of detecting as little as a few parts per billion of 3-(*p*-chlorophenyl)-1,1-dimethylurea in refined cane sugar and a few parts per 10,000,000 in nearly all plant tissues and soils.

RESIDUAL QUANTITIES of the herbicide, 3-(*p*-chlorophenyl)-1,1-dimethylurea (formerly known as CMU, the active ingredient in Du Pont Karmex W herbicide for agricultural use and Du Pont Telvar W weed killer for industrial use) have been determined in soil by a method which involved extraction with a mixture of acetonitrile and acetic acid, hydrolysis of the recovered active ingredient, and colorimetric determination of the resulting *p*-chloroaniline by diazotizing and coupling (*2*). However, this procedure proved unsuitable for determining residual 3-(*p*-chlorophenyl)-1,1-dimethylurea in plant tissues and in certain highly absorptive types of soil. A more general method has been perfected, based on the caustic hydrolysis principles described in the closing paragraphs of the earlier paper and utilized by Young and Gortner (*4*) for determining 3-(*p*-chlorophenyl)-1,1-dimethylurea in pineapple tissue.

In this improved procedure, the residual 3-(*p*-chlorophenyl)-1,1-dimethylurea is quantitatively hydrolyzed to *p*-chloroaniline by refluxing the sample with a concentrated sodium hydroxide solution. The resulting *p*-chloroaniline is recovered from the caustic digestate by a combination of continuous steam distillation and extraction or by liquid-liquid extraction, following which it is determined colorimetrically. Complete recovery of residual 3-(*p*-chlorophenyl)-1,1-dimethylurea has been obtained from all plant tissues and soils examined. Although elapsed time for a single analysis is essentially the same as in the original extraction method, the caustic hydrolysis