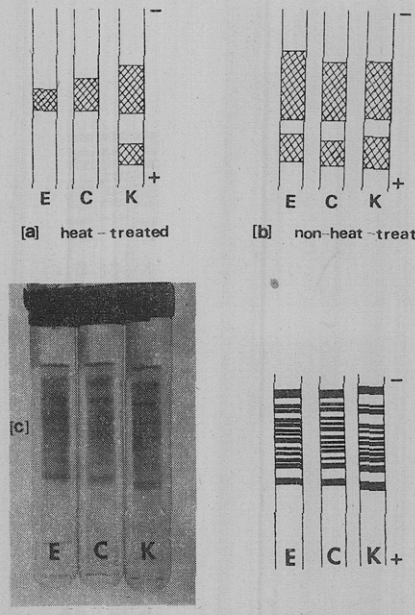

Figure 2. Starch zymograms of (a) crude heat-treated and (b) crude nonheat-treated extracts and (c) gel electrophoretic pattern of nonheat-treated crude extracts. Eagle (E), Clark's Cream (C), KS73256 (K).

other varieties. That was expected because it exhibited the highest level of sprouting damage (Table II) and, according to Kruger (1972a,b), as germination time increases, more α-amylase components become active.

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Comparison of the Amino Acid Composition of Tomato Pulp Recovered from Caustic Peelings to That of Conventionally Processed Tomato Pulp and Fresh Tomatoes

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Tomato pulp recovered from caustic (sodium hydroxide) peelings obtained from commerical peelers has been considered as a potential food material. The nonsulfur amino acids of reacidified recovered pulp were compared to the amino acids of both conventionally processed tomato pulp and fresh tomatoes to determine the extent of modification in composition caused by the exposure to hot alkali. Arginine was the only amino acid that decreased appreciably in the peeling process; the recovered pulp product contained 25–83% of that found in fresh tomatoes, depending upon the severity of the process. This degradation of arginine can be minimized by proper control of process conditions. The decrease in arginine content appears to be a sensitive indicator for the severity of exposure of tomato to alkali.

Tomatoes, like many other fruits and vegetables, are often peeled commercially by immersion in hot caustic solution, followed by removal of the skin and adhering pulp either by spraying with water or by rubbing with rubber disks (Hart et al., 1974). The use of rotating rubber disks to remove peels reduces water consumption and results in peelings that have about the same solids content as whole tomatoes. This byproduct can be discarded, as is the current practice, or the pulp can be economically recovered for food use by acidification and separation of the desirable pulp from the less desirable skin, as reported previously by Schultz et al. (1977).

Alkaline treatment of proteins has been reported to lower their nutritional value (deGroot and Slump, 1969; Gorill and Nicholson, 1972). Alkali and heat converts some of the amino acid residues in proteins to unnatural amino acids and also can cause racemization of amino acid res-

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Table I. Histories and Analyses of Tomato Samples

product (treatment)	no. assayed	NTSS[a]	protein[b]	alkali exposures			NaCl[c]
				pH	temp, °C	min	
fresh, 1975	2		0.84	NA	NA	NA	
fresh, 1976	4	5.1	0.88	NA	NA	NA	0.1
conventional (1975)	2	5.3	0.82	NA	NA	NA	0.1
recover pulp (1975)	6	5.2	0.76	13	44-60	5.5	3.1
recover pulp (1976)	5	5.3	0.92	11	33-38	4-6	1.0

[a] NTSS = percent natural tomato solids: arithmetic mean. [b] Kjeldahl nitrogen × 6.25 = protein on whole product basis. [c] Salt content is primarily from neutralization of NaOH with HCl for recovered pulp product. NA = not applicable.

idues (Cuq et al., 1974; Finley and Friedman, 1977). While many of the detrimental effects of the prolonged alkaline treatments used in the aforementioned studies are not likely to occur with tomatoes under the conditions in the normal tomato peeling process, some modification of amino acid composition of the recovered tomato peel pulp can be expected due to the sensitivity of certain amino acids to alkali and heat. Therefore, it was considered advisable to compare the amino acid composition of the pulp recovered from caustic peelings with that of conventionally processed tomato products and fresh tomato, even though tomato is generally considered a very minor source of protein. This work reports the proximate amino acid composition of fresh and conventionally processed tomato and of representative samples of the recovered pulp product prepared during two seasons under notably different degrees of exposure to alkali.

MATERIALS AND METHODS

Source of Samples. The recovered tomato pulp samples were obtained from two experimental process lines set up at different canneries in 1975 and 1976 (Schultz et al., 1977). In 1975 the recovered pulp samples were prepared by acidifying and screening caustic peelings obtained from a commercial process line (10–30 gal of peelings/min). In 1976 the recovered pulp samples were prepared by acidifying and screening, in a similar manner, the peelings from a pilot peeling line (0.4 gal of peelings/min). In both series of tests the peelings were obtained from tomatoes immersed in hot caustic baths (93–99 °C, 10–12% w/w sodium hydroxide) for 30 s. In all tests the peelings were acidified within 6.5 min of the initial exposure to the caustic bath. The recovered product was filled into 211 × 400 cans, sealed, and processed in boiling water for 40–45 min before cooling in 23 °C water. The samples were stored at 4 °C until analyzed. The actual processing variables are described by Schultz et al. (1977). In 1975 the peelings were obtained from one variety of tomato, VF-145B-7879; in 1976 the samples analyzed were from UC-134 variety tomatoes.

Conventionally processed tomato juice samples were obtained from the regular commercial production line of the processing plant in 1975 and canned in the manner described. The 1975 fresh pulp samples represented peel pulp obtained by manually peeling VF-145B-7879 tomatoes and removing the pulp immediately below the skin. The 1976 fresh pulp samples represented whole UC-134 variety tomatoes that were homogenized with an electric blender. The samples were preserved by lyophilization and/or freezing.

Methods. The total nitrogen content of each sample was determined by the Kjeldahl procedure (AOAC, 1960). Samples (0.50–2.00 g) containing 0.8–2.4 mg of N were hydrolyzed in 6 N HCl, total volume 11–16 mL, for 20 h at 110 °C under high vacuum in sealed flasks as described by Kohler and Palter (1967). Each sample was filtered and analyzed by the accelerated ion-exchange method (Spackman, 1963; Spackman et al., 1958), using a Phoenix Model K-800B or Durrum D-500 automatic amino acid analyzer.

RESULTS AND DISCUSSION

The samples evaluated for this study are shown in Table I, which summarizes some characteristics that describe the type of product (e.g., percent natural tomato soluble solids, NTSS) and the degree of exposure of the recovered pulp products to alkali during processing. The conventional products were neither exposed to alkali nor salted. The sodium chloride content of each recovered pulp product serves as an index of the alkalinity of the peelings used for this product since all recovered pulp was acidified with concentrated hydrochloric acid to pH 4.2 ± 0.1. The mean salt content in the recovered pulp products of 1975 and 1976 was 3.1 and 1.0%, respectively. A level of 1% NaCl is equivalent to about 0.66% NaOH (0.16 N) in the peel pulp. The peelings used in 1975 often had abnormally high caustic concentration and temperature (up to 60 °C) due to hot caustic solution (93–99 °C, 10–12% w/w NaOH) overflowing (improperly) into the collecting trough in the cannery. There was no practicable means of avoiding this unexpected problem during the test period. The high alkalinity resulted in a recovered pulp product with higher salt and lower solids contents than possible if such a condition were avoided. This overflow and excess caustic would not be present in the recovery operation proposed, but it did serve to demonstrate the importance of controlling exposure of the product to caustic in regards to concentration, temperature, and time. The high alkalinity and high temperature experienced in 1975 were not present in 1976 because peelings were obtained from a pilot peeling line which allowed complete control of the peeling process. These (1976) peelings cooled very rapidly and had uniformly low alkali content, as shown by their salt contents (1%).

The arithmetic mean for the protein content (total N × 6.25) of all samples of recovered pulp analyzed from both seasons was 0.81% (wet basis), which is very similar to the 0.81–0.82% found for the samples of conventionally processed juice (1975) and to the 0.8–0.9% reported for canned tomato juice (regular and salt-free) in Agricultural Handbook No. 8 (Watt and Merrill, 1963). The protein content of the recovered pulp product appeared to be slightly higher in 1976 than in 1975 (0.92 vs. 0.76). This difference was due in part to the dilution of the recovered product by the excess caustic solution that spilled into the peelings in 1975.

Representative samples of recovered pulp (1975, 1976), conventionally processed tomato pulp (1975), and fresh tomato pulp (1975 and 1976 data combined) were analyzed for amino acids. The mean content and standard deviation for each of fifteen amino acids are given in Table II for four categories of tomato samples. The results for the fresh tomato samples of 1975 and 1976 were combined since there was no significant difference in their composition. The amino acid composition reported by the Food and Agriculture Organization of the United Nations (1970) for

Table II. Amino Acid Composition of Protein in Tomato Products: Mean Values ($\bar{x}$) of Amino Acid Contents Expressed as g/16 g of N, with Standard Deviations (SD)

amino acid	tomato, FAO (1970)	fresh tomato		conventional product		1975 recov pulp		1976 recov pulp	
		$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
Asp	11.50	16.41	2.93	13.19	1.34	13.24	0.43	17.00	2.78
Thr	2.21	2.46	0.15	2.40	0.09	2.41	0.10	2.72	0.07
Ser	2.50	2.50	0.21	2.51	0.30	2.71	0.11	2.66	0.14
Glu	41.39	37.58	6.56	38.13	3.82	34.59	1.71	40.83	2.12
Pro	1.60	1.72	0.33	1.88	0.01	2.03	0.14	2.07	0.32
Gly	1.79	2.14	0.25	2.30	0.03	2.48	0.11	2.49	0.22
Ala	2.40	3.37	0.49	3.68	0.79	4.31	0.45	3.34	0.38
Val	2.10	1.98	0.72	1.97	0.22	2.11	0.25	2.22	0.22
Ile	1.79	1.82	0.30	2.00	0.06	2.07	0.09	2.13	0.14
Leu	2.70	2.83	0.40	2.92	0.09	3.12	0.08	3.42	0.24
Tyr	1.30	1.56	0.26	1.42	0.12	1.49	0.08	1.78	0.12
Phe	1.79	2.67	0.28	2.32	0.01	2.28	0.08	2.59	0.13
His	1.49	1.51	0.18	1.64	0.11	1.33	0.13	1.52	0.14
Lys	2.80	3.00	0.54	3.07	0.34	3.02	0.14	3.31	0.24
Arg	2.10	1.96	0.21	2.12	0.09	0.49	0.27	1.62	0.28
unknown[a]		6.89 (4)	2.26	6.92 (1)		4.16 (4)	0.81	2.67 (5)	0.82
total (including unknown)		90.40		88.45		81.84		92.37	
no. of samples	1	6		2		6		5	

[a] Calculated as γ-amino butyric acid: The number given in brackets after the estimated quantity of unknown is the number of samples showing the unknown, i.e., the number analyzed with the Durrum analyzer.

the chromatographic analysis of a single sample of tomatoes is included in Table II for comparison. Sulfur amino acids were not determined in the present study. FAO reported that each of the sulfur amino acids, cystine and methionine, occurs at 0.59 g/16 g of N.

Some of the samples were analyzed with a Durrum amino acid analyzer, using a longer development time than in the procedure employed with the Phoenix analyzer; in these samples a prominent unknown peak, believed to be γ-aminobutyric acid, appeared just before the histidine peak. To substantiate that this unknown was γ-aminobutyric acid, its absorption ratio at 440/590 nm was calculated and compared with that observed with a γ-aminobutyric acid standard. The similarity of these ratios, as compared to the ratios for other amino acids, indicated that this unknown was γ-aminobutyric acid. The concentration of the unknown was estimated by calculating the area of the peak as γ-aminobutyric acid; it is included in the results in Table II because it contributes to the total amino acid content (recovery) based on total nitrogen. Several of the samples examined with the Durrum D-500 analyzer had a small ornithine peak ahead of lysine. Ornithine and several unknowns that occurred in minor amounts are not included in Table II.

Except for a noticeably lower level of arginine in one of the two recovered pulp products (i.e., 1975), the amino acid compositions of all sample categories are very similar and, in general, resemble that reported by FAO (1970). A decrease in arginine in the recovered pulp product is not unexpected since arginine has been reported to be the most alkali labile amino acid of the nonsulfur amino acids (Cuq et al., 1974). The amino acid composition of the tomato samples in this study is closer to that reported for tomato by the FAO (1970) than that reported for tomato skin by Tsatsaronis and Boskou (1975), as it should be. Tomato skin appears to contain appreciably more glycine, proline, valine, serine, threonine, and tyrosine, and less glutamic acid than either whole tomato or recovered tomato pulp.

Upon close examination of the data, certain amino acids (e.g., leucine and glycine) appear to have increased slightly in the alkali-treated product relative to the levels found in fresh and conventionally processed tomatoes. de Groot and Slump (1969) reported similar increases for several amino acids in some alkali-treated proteins. Slight increases in certain amino acids could be artifacts due to decomposition products of amino acids that sometimes appear under peaks of normal amino acids (e.g., ornithine may appear as lysine in some analyses). Under harsh conditions it is possible that some amino acid derivatives, such as those reported by Friedman (1977) and by Finley and Friedman (1977), may be formed. Several samples that were examined for lysinoalanine showed little or no increase above the trace of this compound found in conventionally processed tomato products.

Slight increases in stable amino acids relative to total nitrogen can occur as a result of the loss of ammonia during alkaline degradation of labile amino acids. Certain amino acids are degraded under harsh alkaline conditions with concomitant loss of ammonia, so that a decrease in total nitrogen would result in an apparent increase in a stable amino acid. Since total nitrogen can decrease to some extent under alkaline conditions, it seems preferable to express amino acid content of alkali-treated products on the basis of a stable amino acid, or a relatively stable one, rather than on the basis of total nitrogen. For example, the level of a given amino acid in the recovered pulp can be expressed as a ratio of that amino acid to isoleucine since isoleucine showed no significant difference among the treatments.

The effect of alkaline exposure on the amino acid composition of the recovered pulp is examined more closely in Table III in which the samples of recovered pulp from both test series are tabulated according to their degree of exposure to alkali (NaCl content) and compared in respect to several amino acids known to be subject to alkaline degradation. The compositions of fresh tomato and conventionally processed tomato pulp in respect to these same amino acids are included in Table III to represent tomato pulp not exposed to alkali. The amino acid contents are given as molar ratios relative to isoleucine, rather than on a total nitrogen basis, to avoid any discrepancy due to the loss of nitrogen in samples exposed to alkali. The results indicate that the amount of arginine lost is related to the degree of alkaline exposure. Much less degradation of arginine occurred in the recovered pulp prepared in 1976 than in that prepared in 1975 due to the lower alkalinity

Table III. Effect of Alkaline Exposure on Selected Amino Acids in the Recovered Tomato Pulp

tomato sample	alkaline exposure[a] (% NaCl)	ratio of amino acid to isoleucine[b] Arg	Thr	Ser	Lys
fresh					
FP-A		0.71	1.47	1.53	1.34
FP-B		0.69	1.31	1.55	1.52
214	0.1	0.86	1.58	2.02	1.55
262	0.1	0.91	1.85	1.93	1.42
297	0.1	0.94	1.56	1.84	1.49
328	0.1	0.82	1.31	1.55	1.53
mean	0.1	0.82	1.51	1.74	1.48
conventional					
O/LF		0.78	1.39	1.73	1.29
22LJ	0.1	0.80	1.27	1.40	1.46
mean	0.1	0.79	1.33	1.56	1.38
recovered 1976					
76039	0.9	0.69	1.46	1.62	1.36
76013	0.9	0.69	1.48	1.67	1.40
76009	0.9	0.45	1.40	1.52	1.42
76021	1.1	0.45	1.35	1.42	1.41
76017	1.3	0.61	1.36	1.60	1.38
mean	1.0	0.57	1.41	1.57	1.39
recovered 1975					
22A	1.8	0.35	1.35	1.66	1.28
16A	2.8	0.22	1.31	1.70	1.38
15A	2.9	0.21	1.26	1.59	1.30
19A	3.4	0.12	1.26	1.60	1.21
13A	3.7	0.10	1.26	1.60	1.36
19B	3.8	0.08	1.27	1.65	1.34
mean	3.1	0.18	1.28	1.63	1.31

[a] The NaCl content is almost entirely due to the neutralization with HCl (to pH 4.2), and it is, therefore, a measure of the alkalinity of the peelings. The natural salt content of tomatoes is about 0.1%. [b] Molar ratios.

and temperature of the peelings in the second series of tests. Ornithine, a product of arginine degradation, was found in three of four samples of 1975-recovered product analyzed with the Durrum D-500 but in only two of five samples of 1976-recovered product so analyzed. No ornithine was found in samples of fresh tomato and conventionally processed product analyzed with the Durrum D-500. Ornithine was found only in samples having a low arginine/isoleucine ratio, i.e., 0.45 or less; however, there appears to be no quantitative relationship of the ornithine to the arginine remaining in these samples. It is noteworthy that serine and threonine, both of which are reportedly unstable in alkali (Cuq et al., 1974; Friedman, 1978), showed little or no change under the alkaline conditions involved in either of the series of tests.

Since arginine appears to be quite unstable to alkaline conditions in the peeling process, an arginine analysis could be useful as an objective assay of the severity of alkaline exposure sustained by tomato pulp recovered from caustic peelings. Cuq et al. (1974) reported some decrease in arginine under some of the mildest conditions they tested; they observed that the decrease in arginine and the formation of ornithine were the most sensitive indicators for the severity of alkaline treatments to which a protein has been exposed. Since amino acid analysis is a very complex and lengthy procedure, it would clearly not be useful for routine quality control purposes. However, it would be useful as a guide in the development of a suitable process that involves alkaline exposure, or it could be useful as an occasional check on the appropriateness of process conditions.

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