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ABSTRACT

The effects of thermal processing and NaCl addition on the acidity of home canned tomatoes were investigated. Unsalted canned tomatoes were higher in pH and lower in titratable acidity than corresponding raw composites. The latter did not change in acidity prior to analysis. Salt depressed the pH of raw and canned tomatoes. This change was attributed to the well known Debye-Hückel effect.

INTRODUCTION

A RESEARCH PROGRAM has been undertaken at the Eastern Regional Research Center (ERRC) to evaluate the safety of home canned tomatoes with respect to acidity and to determine the feasibility of acidulation to decrease the risk of botulism with low acid tomatoes. The acidity of tomatoes varies greatly, depending not only on variety but also on ripeness and on growing conditions (Sapers et al., 1977). In assessing the safety of home canned tomatoes and determining acidulation requirements, it is important to understand the relationship between raw material acidity and the pH of the canned product.

The effect of thermal processing on tomato acidity is not clear. Kattan et al. (1956) and Lopez et al. (1968) reported no difference in pH between raw tomatoes and corresponding canned products. Hamdy and Gould (1962) observed a decrease in the pH of juice from seven tomato cultivars during thermal processing. Lamb et al. (1962) reported that processing had no effect on the pH of canned tomatoes although their data for unsalted controls show a slight increase in pH due to heating. Stadtman et al. (1976) observed that processed juice is consistently higher in pH than laboratory samples of unprocessed juice from the same lot of tomatoes.

A number of investigators have reported that NaCl and CaCl₂ lower the pH of canned tomatoes (Powers, 1976). The effect of the latter compound has been attributed to a shift in the equilibrium between Ca⁺⁺ and calcium citrate due to the presence of added CaCl₂, i.e., the common ion effect (Lopez et al., 1968). However, the pH lowering effect of NaCl has not been explained.

The objective of the research reported herein was to determine the effects of thermal processing and salt addition on the pH and acidity of home canned tomatoes and the relationship of these effects to product safety.

EXPERIMENTAL**Materials**

Ace 55 VF, Big Girl, Jet Star, Manalucie and San Marzano tomatoes were harvested at Fordhook Farms, the W. Atlee Burpee Company Experiment Station located in Doylestown, PA. Ace and Cal Ace tomatoes were obtained from the Michigan State University farm at Sodus, MI. Valiant tomatoes were provided by Mississippi State University. All

tomatoes were stored at room temperature until table ripe with the exception of the highest pH Ace 55 VF sample which was harvested in an over-ripe (but unblemished) condition.

Canning

Tomato samples were canned by a modification of the USDA raw pack procedure (USDA, 1975). Tomatoes were peeled after being dipped in boiling water for 1 min. The peeled trimmed tomatoes were cut into eighths, one piece being added to each of seven pint canning jars and the remaining piece being added to a Waring Blendor jar. This procedure was repeated until the jars were filled to a net weight of 450g. Individual jars within each set of seven were either unsalted or salted by the addition of 0.667% NaCl equivalent to 3g or approximately ½ teaspoon per pint, the level specified in the USDA procedure. A few samples were salted by the addition of 2.0g NaCl per pint (0.444%), equivalent to the salt content of a commercial acidulant tablet developed for home canners (Morton Salt Co., Chicago, IL). Jars were closed with metal screwbands and flat metal lids. All products were processed in a boiling water bath for 35 min. Raw pieces in the blendor jar, representing a composite of the canned product, were blended and analyzed as soon as the jars were filled (approximately 30 min after the start of raw material preparation). The canned products were stored at room temperature for one month prior to analysis.

Analyses

Raw composites were blended for 2 min and analyzed for pH and titratable acidity (T.A.) as described by Sapers et al. (1977). Canned products were blended for 30 sec at high speed with a Waring Blendor and were then analyzed for pH and T.A. All pH measurements with raw and canned tomatoes were made with a standard glass electrode immersed in an unstirred sample, with the expanded scale of the pH meter. The significance of differences in pH and titratable acidity between thermally processed, salted, unsalted, and raw samples was determined by means of the paired t-test.

RESULTS & DISCUSSION**Effect of thermal processing on pH and T.A.**

Measurements of pH and T.A. were made on 13 sets of unsalted canned tomatoes and corresponding raw composites representing 8 high and low acid varieties. The canned products were significantly higher in pH and lower in T.A. than were the raw tomatoes (Table 1). pH values were elevated by as much as 0.1 unit in some canned samples. The magnitude of these changes appears to be unrelated to variety, ripeness, the T.A. or pH values of the samples, or product storage. Similar results were obtained with products equilibrated for 1–3 days and with products stored for one month prior to analysis.

Stadtman et al. (1976) attributed the difference in pH and T.A. between processed and unprocessed juice to enzymatic changes in the unprocessed juice rather than to heat-induced changes or the loss of volatile acids in the processed juice. We varied sample preparation times for raw tomatoes to determine whether pH and T.A. values changed under the conditions used to prepare composite samples during canning. Holding of the blended and the unblended composites for as long as 30 min prior to analysis did not affect pH or T.A. Similarly, a reduction in blending time from 2 to 1 min (shorter blending times result in inadequate comminution) had no effect on pH or T.A., suggesting that rapid enzymatic changes during blending were not involved. Consequently, we believe that the

Table 1—Effect of home canning on pH and titratable acidity of unsalted tomatoes.

Variety	Raw composite		Canned product		Difference ^b	
	pH	T.A. ^a	pH	T.A. ^a	ΔpH	ΔT.A. ^a
Ace	4.44	0.385	4.54	0.356	+0.10	-0.029
Ace 55 VF	4.66 ^c	0.212 ^c	4.73 ^c	0.237 ^c	+0.07 ^c	+0.025 ^c
	4.52	0.280	4.60	0.276	+0.08	-0.004
	4.48	0.322	4.52	0.284	+0.04	-0.038
Big Girl	4.37	0.358	4.37	0.319	0.00	-0.039
	4.31	0.371	4.43	0.316	+0.12	-0.055
	4.30	0.406	4.36	0.425	+0.06	+0.019
Cal Ace	4.42	0.378	4.51	0.358	+0.09	-0.020
Jet Star	4.34	0.358	4.44	0.335	+0.10	-0.023
	4.27	0.365	4.31	0.305	+0.04	-0.060
Manalucie	4.31	0.363	4.41	0.319	+0.10	-0.044
San Marzano	4.49	0.288	4.58	0.265	+0.09	-0.023
Valiant	4.31	0.417	4.37	0.398	+0.06	-0.019
			Mean		+0.07 ^d	-0.024 ^e

^a T.A. = titratable acidity, calculated as % citric acid.

^b Difference = Canned product - Raw composite.

^c Over-ripe sample; all other samples table-ripe

^d Difference significant at 0.001 by Student's t-test

^e Difference significant at 0.01 by Student's t-test

difference in pH and T.A. between raw and canned tomatoes is not due to enzymatic changes in the raw tomatoes but may result from heat-induced changes during thermal processing. Hamdy and Gould (1962) reported a decrease in citric acid and increases in amino N and alpha-keto glutaric acid in eight tomato varieties due to processing. El Miladi et al. (1969) observed increases in citric, malic and pyrrolidone-carboxylic acids and in a number of amino acids in processed tomato juice. Changes in the concentrations of these buffers due to processing can be expected to change the tomato pH (Paulson and Stevens, 1974), although the system is not sufficiently characterized to predict the direction and extent of change.

Effect of salt on pH and T.A.

The addition of salt to home canned tomatoes at the recommended level depressed the product pH relative to that of an unsalted sample by almost 0.1 unit (Table 2). This was accompanied by a very small increase in T.A. As with the thermal processing effect, the salt-induced changes were not related to variety, ripeness or the sample pH value or T.A. Since the salt effect is similar in magnitude but opposite in direction to the processing effect, there was little difference in pH and T.A. between raw composites and salted products.

The salt effect was observed with raw tomatoes, blended

Table 3—Effect of sodium chloride level on tomato pH and titratable acidity

Variety and treatment	pH			T.A. ^a		
	% NaCl			% NaCl		
	0	0.444 ^b	0.667 ^c	0	0.444 ^b	0.667 ^c
Ace 55 VF						
Raw	4.27	4.18	4.15	0.366	0.379	0.380
Canned	4.36	4.30	4.29	0.329	0.327	0.333
San Marzano						
Raw	4.21	4.13	4.12	0.441	0.443	0.444
Valiant						
Raw	4.25	4.18	4.17	0.516	0.519	0.512

^a T.A. = titratable acidity, calculated as % citric acid.

^b Equivalent to Morton Salt Company acidulant tablets

^c Equivalent to USDA recommendation of ½ teaspoon/pint

Table 2—Effect of sodium chloride on pH and titratable acidity of home canned tomatoes

Variety	Difference between salted product ^a and					
	Raw composite		Raw composite		Unsalted product	
	pH	T.A. ^b	ΔpH	ΔT.A. ^b	ΔpH	ΔT.A. ^b
Ace	4.44	0.385	+0.01	-0.016	-0.09	+0.013
Ace 55 VF	4.66 ^c	0.212 ^c	-0.07 ^c	+0.029 ^c	-0.14 ^c	+0.004 ^c
	4.52	0.280	-0.02	-0.011	-0.10	-0.007
Big Girl	4.37	0.358	-0.03	-0.033	-0.03	+0.006
	4.31	0.371	+0.01	-0.041	-0.11	+0.014
	4.30	0.406	-0.03	+0.039	-0.09	+0.020
Cal Ace	4.42	0.378	-0.02	-0.014	-0.11	+0.006
Jet Star	4.34	0.358	+0.01	-0.027	-0.09	-0.004
	4.27	0.365	-0.04	-0.050	-0.08	+0.010
Manalucie	4.31	0.363	+0.01	-0.043	-0.09	+0.001
San Marzano	4.49	0.288	-0.01	-0.008	-0.10	+0.015
Valiant	4.31	0.417	-0.03	-0.019	-0.09	0.000
	Mean		-0.02 ^e	-0.016	-0.09 ^d	+0.006 ^e

^a 3.0g NaCl per pint (0.667%)

^b T.A. = titratable acidity, calculated as % citric acid.

^c Over-ripe sample; all other samples table-ripe

^d Difference significant at 0.001 by Student's t-test

^e Difference significant at 0.05 but not 0.01 by Student's t-test

for 2 min at high speed prior to the addition of salt, as well as with canned tomatoes, and was similar at two different levels of salt addition (Table 3). In these experiments, salt depressed the tomato pH but had no measurable effect on T.A. We obtained similar results by adding salt to raw tomato serum, prepared by centrifugation, as well as to the blended raw tomato. The salt effect also occurred when NaCl was added to canned unsalted tomatoes, the pH reduction being similar to that observed with a corresponding product canned with salt. These observations indicate that the pH depressing effect of salt occurs rapidly, is independent of thermal processing effects, and does not involve the solubilization of acidic tomato constituents.

Finally, we were able to demonstrate that the salt effect occurs in citric acid solutions, similar in concentration to the titratable acidity of tomatoes and adjusted with concentrated KOH solution to a pH typical of tomatoes. The pH of such solutions was lowered 0.15–0.17 units by the addition of 0.667% NaCl (Table 4). We believe that this result and the salt effect in raw and canned tomatoes can be explained by the well known Debye-Hückel equation, which predicts an increase in the dissociation of an acid with increasing ionic strength (Freiser and Fernando, 1963).

Table 4—Effect of sodium chloride on pH of citric acid solutions pre-adjusted to pH 4.4

% Citric acid	pH		
	After adjustment ^a	After adding NaCl ^b	Difference ^c
0.2	4.39	4.23	-0.16
	4.44	4.29	-0.15
0.4	4.41	4.25	-0.16
	4.40	4.23	-0.17
0.6	4.40	4.25	-0.15
	4.39	4.22	-0.17

^a Adjusted with conc KOH to pH 4.4

^b 0.667% equivalent to USDA recommendation of ½ teaspoon/pint

^c Difference = pH with NaCl - pH without NaCl.

Implications for home canners

Our observation that thermal processing elevates the pH of raw tomatoes and that salt depresses pH by a similar amount has implications with respect to the safety of home canned tomatoes. The suitability of tomatoes for canning depends in part on their level of acidity, pH values of 4.8 or higher being considered potentially dangerous because of the ability of *Clostridium botulinum* to grow and produce toxin at that pH (Townsend et al., 1954). To provide some margin of safety, the FDA has proposed that a pH value of 4.6 be used as the upper limit for canned foods which are to be made exempt from the provisions of 21 CFR Part 128b, the regulation governing the thermal processing of low-acid foods (Gardner, 1976). A home canner who processes marginally low-acid tomatoes (i.e., having a pH between 4.6 and 4.7) and inadvertently or intentionally omits salt may produce a canned product exceeding pH 4.8. A situation approaching this condition is seen in Table 1 with over-ripe Ace 55 VF tomatoes, the pH being shifted from the 4.66 to 4.73 by thermal processing. We believe that this phenomenon as well as the normal variability of tomato acidity made the FDA safety factor of 0.2 pH unit also relevant to tomatoes for home canning.

Research on the occurrence of low-acid tomatoes and on the feasibility of acidifying home canned tomatoes to provide a greater margin of safety is in progress in our laboratory and will be reported subsequently.

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