INFLUENCE OF DIFFERENT ORGANIC ACIDS ON THE FIRMNESS OF FRESH-PACK PICKLES

INTRODUCTION

CRISP TEXTURE of cucumber pickles is an important quality characteristic. This applies to items prepared from brine-stock, or those from green cucumbers, called "fresh-pack" or pasteurized pickles. The role of pectinolytic enzymes as the cause of cucumber softening during brine fermentation has been thoroughly investigated (Bell et al., 1950; Etchells et al., 1955, 1958a) and methods of control have been suggested (Etchells et al., 1955, 1958b; Bell et al., 1955, 1965). However, texture deterioration of pickle products by nonenzymatic reactions, such as by acids, salts and other chemicals, has been given little attention. Lesley and Cruess (1928) and Fabian and Johnson (1938) suggested that the natural organic acids produced in low-salt content fermentations, such as during the manufacture of genuine dill pickles, were in part responsible for reducing the texture of the final product. Texture loss of pickles at elevated storage temperatures (86°F and above) has been reported for processed dills (Pangborn et al., 1959) and for fresh-pack items (Nicholas and Pflug, 1960).

Monroe et al. (1969) reviewed the development of fresh-pack pickles in this country. They reported that the annual volume of these products requires over 40% of the crop of more than 20 million bushels of pickling cucumbers. They also reported on the influence of acetic acid (range 0.20–1.00%) and internal-product pasteurization temperatures (range 120–200°F) on physical, chemical and microbial changes in fresh-pack dill pickles. They concluded that higher temperatures, from 170–200°F, produced bloater (hollow cucumbers) damage; also, faster heating rates decreased pickle firmness, particularly in the top part of the jar. Etchells and Jones (1942) pasteurized fresh-pack sweet slices and fresh-pack dills and noted that they retained most of their original crispness for 8 months. These products, with equilibrated acidities of 0.4–1.7% acetic acid were pasteurized at an internal-product temperature of 165°F for 15 min, followed by prompt cooling to below 90°F. Recently, Etchells et al. (1972) investigated the effect of alum on fresh-pack dill pickles; they found that alum caused a reduction in firmness of the product during storage. This finding was contrary to the widely accepted belief that alum functions as a firming agent in pickle products.

In the manufacture of fresh-pack pickle products, the cover-brine is poured on packed jars of whole or sliced cucumbers just before capping and pasteurizing. The conventional acidulant in pickle manufacture is acetic acid (vinegar), even though other food-grade acids have been suggested (Sausville, 1965). It is added in the cover-brine at a strength calculated to give the desired equilibrated acid concentration. This usually amounts to 35–40% of the cover-brine concentration. Fabian and Wadsworth (1939) found that acetic acid equilibrated more rapidly than lactic in products made with salt-stock. Also, the rate was greatest for both acids during the first 24 hr.

The experiments herein were designed to exert certain physical and chemical stresses on cucumber texture, some of which exceeded those encountered in the pickle industry. Areas of study were: (a) rate of acid-cucumber equilibration with acetic, lactic, citric and oxalic acids; (b) influence of increasing pasteurization (165°F) "holding-times" on the texture of cucumbers packed and equilibrated for 24 hr in water, acetic or lactic acids; (c) firmness of pasteurized cucumbers as influenced by five organic acids; and, (d) lactic acid-softening of cucumbers.

EXPERIMENTAL

CERTIFIED reagent-grade acetic, lactic, citric, malic and oxalic acids were used. The liquid portion of a jar's content is referred to as the "brine" or the "pickle brine;" but, at the time of addition, it is called the "cover-brine." Each acid was incorporated into the cover-brine and determined (w/v) by titrating a 10-ml sample with a 0.111N NaOH solution to pH 7.5 as measured with a Beckman Zeromatic meter. Acid titrations of the cover-brine at time intervals were used to calculate the percent equilibration. The pickle-brine pH was measured with a Beckman Expandomatic meter. The NaCl content of the cover-brines was determined by the method described by Etchells et al. (1964).

Experimental packs for each series were prepared from freshly-harvested cucumbers, carefully graded to size. The pickling varieties used, Model and SMR-58, were obtained from a pickling company in North Carolina. For each series, the cucumbers were thoroughly washed with tap water and regraded; then, 12–15, 1-1/8 to 1-3/8 in. diam cucumbers were weighed (550–560g) and carefully hand-packed into each 32-oz jar. The cover-brine for each jar measured about 370 ml. This gave a ratio of close to 60% solids and 40% brine by weight. The jars were capped with 70 mm, 4-lug, "twist-off" caps (White Cap Co., Chicago, Ill.) and were pasteurized immediately or after a given equilibration period. The laboratory pasteurization was essentially as that described for a hot water, batch operation (Etchells and Jones, 1944). The experimental packs were stored at about 78°F. Cucumber firmness was determined with a USDA Fruit Pressure Tester (Magness and Taylor, 1925) using the procedure of Bell et al. (1955). The firmness, in pounds, was the average of the center punch values for 10 cucumbers, using a 5/16 in. diam plunger tip. The rating scale used was: 18 lb and above = very firm; 14–17 = firm;

Table 1—Rate of acid equilibration between the cover-brine and whole cucumbers[a]

	5% Acetic acid		1% Lactic acid		1% Citric acid		.4% Oxalic acid	
Time (hr)	pH	Equilibration in %	pH	Equilibration in %	pH	Equilibration in %	pH	Equilibration in %
0.0	2.85	0	2.70	0	2.65	0	2.20	0
1.0	3.05	16	3.00	24	2.85	12	2.40	40
2.5	3.35	40	3.25	38	3.10	28	2.85	65
5.0	3.42	52	3.40	49	3.25	33	3.05	70
10.0	3.65	70	3.60	69	3.50	48	3.45	82
24.0	3.65	85	3.65	79	3.60	64	3.70	88
50.0	3.75	95	3.75	90	3.80	76	3.90	93

[a]The jars contained close to 60% cucumbers and 40% brine on a weight basis.

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[2] H. W. Madison Co., Div. of the J. M. Smucker Co., Medina, OH 44256

Table 2—Influence of increasing pasteurization (165°F) holding-times on the firmness of cucumbers packed in water, acetic or lactic acids

Treatment	Firmness of cucumbers (PT)[a], packed and equilibrated in:					
	Water[c]		Acetic acid[c]		Lactic acid[c]	
	lb	Rating	lb	Rating	lb	Rating
No heat control	19.3	V. firm	15.8	Firm	17.9	Firm
Time held at 165°F[b]						
0 min	18.0	Firm	14.7	Firm	17.1	Firm
15 min	18.0	Firm	15.5	Firm	17.0	Firm
30 min	17.6	Firm	13.9	Firm	14.8	Firm
60 min	16.8	Firm	12.8	Inferior	13.5	Inferior
120 min	14.5	Firm	12.4	Inferior	11.3	Inferior
180 min	12.6	Inferior	9.5	Soft	9.1	Soft
240 min	13.1	Inferior	8.6	Soft	7.7	Soft

[a]For rating scales of the pressure test values and adjective ratings, see EXPERIMENTAL section.
[b]Come-up time for 1-qt jars of cucumbers, from 90°–165°F was 35 min in the hot-water bath.
[c]The equilibrated pH's of the three cover-liquids were as follows: water, 5.8; acetic acid, 3.7; lactic acid, 3.7.

11–13 = inferior; 5–10 = soft; 4 and below = mushy.

RESULTS & DISCUSSION

Rate of acid-cucumber equilibration

Acetic, lactic, citric and oxalic acids were each added separately in the cover-brines to whole cucumbers (Model variety) in amounts calculated to give an equilibrium pH of about 4.0. The results of the tests are shown in Table 1. Oxalic acid equilibrated at the fastest rate, followed by acetic. Citric acid penetrated at the slowest rate, and after 5 hr was only one-third equilibrated, whereas oxalic acid was more than two-thirds, and acetic and lactic acids about one-half. The rate of acid equilibration is an exponential function; plots of percent acid equilibration against log-time (hours) resulted in fairly straight lines for the four acids. Even so, complete equilibration may take as long as 2 or 3 wk. However, acetic, lactic and oxalic, were about 90% equilibrated in 50 hr. In a commercial operation, the jars of pickles reach the steam pasteurizer in a very short time after the cover-brine is added. Thus, little acid penetration occurs before the heating starts.

Increasing pasteurization (165°F) holding-times with cucumbers packed in water, acetic or lactic acids

The experiments were designed to determine the influence of a fixed internal-product pasteurization temperature (165°F), for 0, 15, 30, 60, 120, 180 and 240 min before cooling on the firmness of cucumbers that have been equilibrated in water, acetic, or lactic acid for 24 hr. Cucumber firmness together with the adjective ratings are shown in Table 2. The highest rating, 19.3 lb was for the no heat, water control treatment. Lactic and acetic acids reduced the firmness by two or three pounds during the equilibration period prior to pasteurization. The water-pack cucumbers retained their firmness during the pasteurization treatments better than those acidified with acetic or lactic acid. Further, water-pack-treated stock was still firm at 120 min, whereas cucumbers from the acetic and lactic acid treatments were down to an inferior rating. Cucumbers from both acid treatments were soft after 180 min.

The effect of acid on cucumber texture could be important, considering the actual degree of equilibration of acid and cucumbers before pasteurization. Apparently, from a texture standpoint, it is better not to have the acid fully equilibrated with the cucumbers at the time of pasteurization.

Firmness of pasteurized cucumbers as influenced by different organic acids

Lactic, citric, malic and oxalic were compared with acetic in cucumber-pasteurization and storage tests (Table 3). All but oxalic acid are commonly used in

Table 3—Acidity and pH of the cover-brines and equilibrated pickle brines, and cucumber firmness from five organic acid treatments

Treatment of cucumbers (desired acidity at equilibration)[a]	Initial cover-brine		Examination at:						Increase in acidity at[c]	
			4 months			8 months			4 months	8 months
	pH	% acid	pH	% acid	lb (PT)[b]	pH	% acid	lb (PT)[b]	%	%
Acetic acid										
2%	2.80	4.94	3.92	2.05	15.8	3.75	2.12	14.3	3	6
4%	2.70	9.89	3.70	4.11	12.5	3.50	4.23	10.4	3	6
Lactic acid										
0.4%	2.80	1.02	4.10	0.47	15.3	3.80	0.56	13.2	18	40
0.8%	2.60	1.97	3.78	0.89	8.6	3.60	1.07	9.5	11	34
Citric acid										
0.4%	2.60	1.00	4.30	0.45	15.7	4.05	0.50	14.2	12	25
0.8%	2.45	2.03	3.75	0.82	9.4	3.55	0.89	7.8	3	11
Malic acid										
0.4%	2.65	1.03	4.15	0.45	15.7	3.90	0.51	13.4	12	27
0.8%	2.50	1.93	3.80	0.83	8.9	3.35	0.83	5.5	4	4
Oxalic acid										
0.16%	2.15	0.40	4.40	0.21	< 3	4.15	0.26	< 3	31	62
0.32%	1.95	0.80	3.65	0.36	< 3	3.50	0.40	< 3	12	25

[a]Model variety cucumbers, 1-1/8 to 1-3/8 in. diam size, packed in 1-qt glass jars. Acid treatments are % (w/v) for each acid and added to equilibrate at the desired acidity.
[b]Pressure test: See EXPERIMENTAL section for details.
[c]Increase in titratable acidity for each treatment is the percent increase from the calculated equilibrated concentration shown under "Treatment of cucumbers."

food products. Oxalic acid was chosen because of its calcium and magnesium sequestering properties. The first lot was made to equilibrate at about pH 4.0. In the second, the acid concentrations were twice those of the first. Samples were analyzed after 4- and 8-months' storage. Firmness values are given in Table 3. The lowest levels of acetic, lactic, citric and malic acids gave pressure test values of 15.3–15.8 lb (= firm) after 4-months' storage. After 8 months, the acetic and citric acid treatments were about 1.5 lb lower, and the lactic and malic acid treatments were more than 2 lb lower than at 4 months. When acid concentrations were doubled, all firmness ratings but one dropped to soft (8.6–9.4 lb). The exception was acetic acid which dropped 3 lb to a rating of inferior to soft. To emphasize the effect on texture, the acetic acid concentrations selected (2.0 and 4.0%) were on the very high-side of that used by industry (range 0.6–2.2%). However, results in Table 3 indicate that acetic acid caused the least loss in firmness, followed by lactic, citric, malic and oxalic acids.

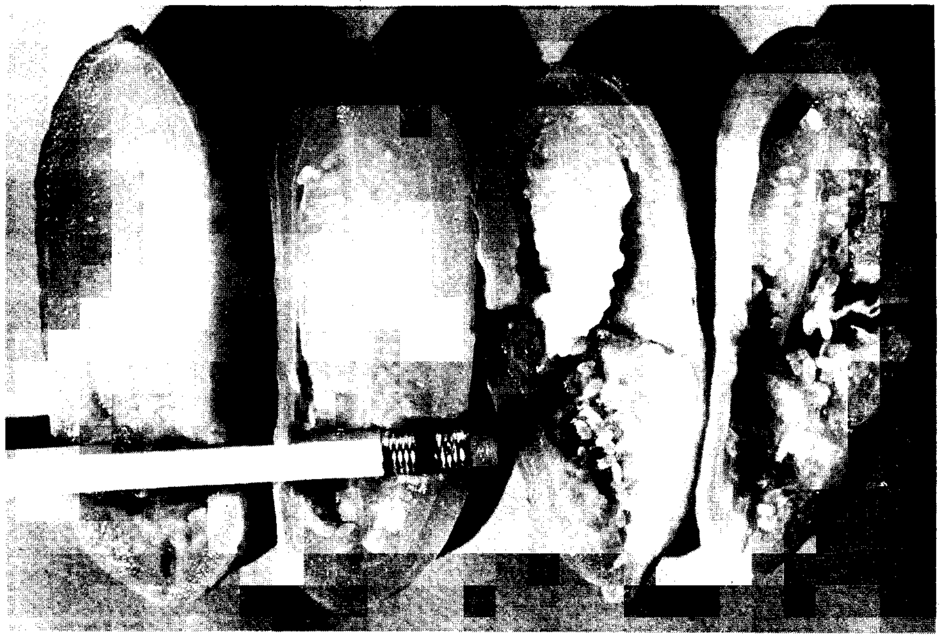

Fig. 1—Cucumber pickles from 1.0% lactic acid experimental fresh-pack after 15 months' storage at room temperature. The soft tissue is illustrated by the ease in which the pencil presses into the cucumber.

Oxalic acid reduced the cucumbers to mush. The stability constants, log K, for Ca^{++} for the acids are as follows: acetic, 0.53; lactic, 1.07; malic, 1.80; oxalic, 3.0; and citric, 3.50. If one accepts that the primary loss of cucumber texture is caused by the shift in calcium from the pectic substances between the plant cells (Matz, 1962; Hulme, 1970), then an explanation is possible for the texture loss by each of the five acids. Acetic acid is weakly dissociated at pH 4.0 (15%), as compared to lactic acid (61%), malic (80%), citric (88%) and oxalic (95%). This was reflected in the individual acid concentrations required to equilibrate at about pH 4.0 (Table 3). Further evidence of the chelating properties as influenced by pH was suggested by Chaberek and Martell (1959). They reported that citric acid is considerably more efficient in the pH range 7–11, requiring an average of two moles of citric acid to one mole of Ca^{++}, whereas, at pH 5 and below, the ratio is greater than ten to one. This explains in part the rather high degree of cucumber firmness (Table 3) for the citric acid treatment at pH 4.

Table 3 also reveals phenomena not completely understood by the authors. During storage, acidity increased, pH values were depressed and cucumber firmness ratings decreased significantly in all treatments except acetic, which exhibited only minor acidity increases. This is especially puzzling because all treatments were acidified and pasteurized in accord with recommended procedures. Furthermore, no signs of fermentation were apparent. Since the acidity and pH levels of acetic acid treatments remained relatively stable, chemical changes associated with softening process may have been a factor in the increased acidity; because, the greatest changes in acidity were associated with corresponding increased losses in firmness.

Lactic acid-softening of cucumbers

In the previous experiment, 0.8% lactic acid caused cucumber softening after

Table 4—Chemical analyses of pickle brines and firmness of pasteurized cucumbers acidified with lactic acid

Treatment of cucumbers (desired acidity at equilibration)[a]	Chemical analyses of pickle brine at:						Cucumber firmness (PT)[b] at			
	3 months pH	15 months pH	3 months % acid[c]	15 months % acid[c]	3 months % NaCl	15 months % NaCl	3 months lb	3 months Rating	15 months lb	15 months Rating
Lactic acid										
0.2%	3.88	3.75	0.26 (30%)	0.30 (50%)	2.20	2.01	14.8	Firm	9.1	Soft
0.4%	3.55	3.46	0.46 (15%)	0.52 (30%)	2.10	1.96	14.0	Firm	8.4	Soft
0.6%	3.28	3.25	0.69 (15%)	0.76 (27%)	2.05	2.04	11.9	Inferior	4.0	Mushy
0.8%	3.18	3.09	0.90 (12%)	1.00 (25%)	2.10	1.98	9.2	Soft	<3.0	Mushy
1.0%	3.10	3.01	1.09 (9%)	1.21 (21%)	2.30	2.02	6.2	Soft	<3.0	Mushy
Acetic acid (control)										
2.0%	3.45	3.34	1.96	1.99	2.10	2.06	13.1	Inferior	6.7	Soft

[a]SMR-58 variety cucumbers, 1-1/8 to 1-3/8 in. diam and packed in 1-qt glass jars. Cover-brines contained 5g/100 ml NaCl; 0.5, 1.0, 1.5, 2.0 and 2.5g/100 ml lactic acid; and 5.0g/100 ml acetic acid. Pack-out ratio was close to 60% cucumbers and 40% brine by weight.
[b]Pressure test: see EXPERIMENTAL section for details.
[c]Values in parentheses are % increase in titratable acidity for each acid treatment (see Table 3, footnote c).

only 4 months' storage. Lactic acid is one of the important acids in pickling, particularly in the natural fermentation of cucumbers for salt-stock pickles (Etchells et al., 1964) where it is the major acid produced. Consequently, five levels of lactic acid were evaluated as to their influence on firmness of cucumbers (Table 4); a 2.0% acetic acid control lot was included.

Cucumber firmness measurements after 3 months' storage clearly show the softening action of lactic acid. The two low levels, 0.2 and 0.4%, resulted in firm cucumbers, but cucumbers at the two high levels, 0.8 and 1.0%, were soft. This type of softening-spoilage is illustrated in Figure 1. Firmness of cucumbers in the acetic acid control was reduced to inferior at 3 months and soft at 15 months. However, in commercial practice, the equilibrated brine acidities would usually fall in the 0.60–1.5% range, not 2.0%.

Chemical analyses of the brine at 3 and 15 months again showed an increase in acidity of the soft lots accompanied by a drop in brine pH.

The 5% NaCl added in the cover-brine of the five lactic acid treatments equilibrated in the jars containing cucumbers at an average of 2.1 and 2.0% at 3 and 15 months, respectively. Sodium chloride was calculated to equilibrate at 2.0%, hence, variability in the pack-out ratio of cucumbers and cover-brine for each sample was small (Table 4). The addition of NaCl to the test-pack depressed the pH values as compared to the same lactic acid treatments without salt (Table 3). The salt apparently had no effect on the lactic acid softening.

In conclusion, the results reported preclude the use of lactic, citric, malic, or oxalic acids in the manufacture of fresh-pack pickles. Acetic acid (vinegar) (0.6–1.5%) was the acidulant that produced the best-textured fresh-pack pickle products.

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