such systems. In other types of aqueous preparation with 10% Tween-80, which does not offer protection to vitamin A, high concentrations of surface active agent may affect the molecular orientation and make vitamin A readily accessible to radiation damage.

These results reveal that, in addition to the effects of solvent and concentration of molecule, the mode of dispersion is important in determining the radiation response of vitamin A. Thus, our evidence points to one protective factor, occurrence of which in foods may be important in the consideration of radiation damage to compounds which are labile in the isolated state. Such and other protective mechanisms will tend to reduce the possibility of food toxicity arising from radiation degradation products.

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Temperature and Storage Effects on Percent Retention and Percent U.S. Recommended Dietary Allowance of Vitamin C in Canned Single-Strength Orange Juice

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Canned single-strength orange juice stored at 29.4, 37.8, and 46.1 °C for 12 weeks showed that the log % vitamin C retention was linearly related with time at 29 °C but not at 38 or 46 °C. Storage of 14 processed juices at 4.4 to 48.9 °C over 12 weeks showed that temperatures greater than ca. 27 °C markedly decreased the rate of vitamin C retention. Orthogonal polynomials were used to determine the equation for vitamin C degradation over 29.4 to 48.9 °C.

A major nutritional value of citrus fruit is their vitamin C content. Many nutritionists consider a daily intake of 50 to 150 mg per day is needed for good health maintenance. The National Academy of Sciences (Food and Nutrition Board, 1974) has recommended a daily intake of from 35 mg (infants) to 80 mg (lactating females) whereas the Food and Drug Administration (FDA, 1973) considers an intake of 60 mg per day (for adults and children 4 years or more in age) as meeting the 100% U.S. RDA requirement.

The retention of vitamin C potency in citrus products is important both to the consumer, concerned with maintaining good health, and to the citrus processor. Because of intensified interest in nutrient labeling, the citrus processor is concerned with the vitamin C content, which is expressed as percent U.S. RDA value, in orange juice products and it's change during product storage.

Many studies (Moschette et al., 1947; Sheft et al., 1949; Freed et al., 1949; Blundstone et al., 1971; Bissett and Berry, 1975) have shown loss of vitamin C in single-strength orange juice (SSOJ) was related to storage temperatures. High-temperature loss of vitamin C may result from processing, unfavorable heat dissipation of the freshly processed juice (stack-burn), warehouse storage (heat pockets, poor air circulation, improper insulation), poor transit conditions (over-heated tractor trailers, railway cars, etc.), and poor handling at distribution centers and supermarkets (lack of rotation of flavor-sensitive foods).

A comparative study of the rates of vitamin C degradation at both low and high storage temperatures has

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Table I. Some Chemical and Nutritional Properties of Freshly Processed Single-Strength Orange Juice

Season	Plant	pH	% citric acid	° Brix	° Brix acid	Vitamin C mg/6 fluid oz	Vitamin C % U.S. RDA[a]
Early	A	3.67	0.80	10.7	13.4	86.3	144
	B	3.69	0.77	10.2	13.2	80.3	134
	C	3.54	0.98	10.4	10.6	89.7	150
Mid	A	3.67	0.96	12.6	13.1	104.8	175
	B	3.52	1.11	11.9	10.7	89.4	149
	C	3.68	0.92	11.6	12.6	98.1	164
Early-Valencia	A	3.58	1.02	11.1	10.9	84.2	140
	B	3.64	0.95	11.0	11.6	71.2	119
	C	3.63	0.88	10.7	12.2	74.8	125
	D	3.58	1.01	11.1	11.0	86.3	144
Late-Valencia	A	3.79	0.79	11.1	14.1	68.7	115
	B	3.88	0.77	12.4	16.1	55.4	92
	C	3.78	0.80	12.2	15.3	73.0	122
	D	3.83	0.79	11.8	14.9	67.6	113

[a] 60 mg of vitamin C/6 fluid oz equals 100% U.S. RDA; 1 fluid oz equals 29.57 ml; therefore, 100% U.S. RDA in metric equivalent is 60 mg of vitamin C/177.4 ml.

apparently not been undertaken. Such a study could help predict future problems in vitamin C loss in commercial citrus juices.

We conducted the present study to determine effects of both low and high temperatures on retention of vitamin C and on changes in percent U.S. RDA values of standard 6 fluid oz portions of canned SSOJ. Tests were conducted over a 12-week period on commercial canned SSOJ prepared during the 1972–1973 processing season.

EXPERIMENTAL SECTION

Materials. Commercially processed, canned SSOJ was obtained from three processors (A, B, C) during the early season (November to January, mostly Hamlin orange juice) and mid-season (January to March, mostly Pineapple orange juice) and from four processors (A, B, C, D) during the early-Valencia season (April–May) and late-Valencia season (May–July). SSOJ in 46-oz cans was taken directly from the production lines in the processing plants and placed in a laboratory locker at −18 °C.

Methods. Degrees Brix, degrees Brix/acid, and percent citric acid were determined by official analytical methods (AOAC, 1970). Vitamin C was determined according to the potentiometric procedure of Spaeth et al. (1962). The method was selected because it is more precise and reproducible than the colorimetric AOAC method which is subject to error in end-point recognition. The method is also ideal for highly colored fruit juices (citrus, tomato, grape). SSOJ samples were stored in temperature-controlled chambers. All Fahrenheit temperatures have been changed to correspond to Celsius temperatures. All retention studies are based on the vitamin C value (100%) for the canned product at zero time (vitamin C of juice measured immediately after canning). For the study of percent vitamin C retention vs. storage time, late-Valencia juice from plant C was monitored bi-weekly for 12 weeks at 29.4, 37.8, and 46.1 °C. In a second study, 14 SSOJ samples (one from each of the processors for each season) were analyzed for vitamin C retention after 12-weeks storage. Fourteen cans were stored at each temperature, viz., 4.4, 15.6, 21.1, 29.4, 32.2, 35, 37.8, 40.6, 43.3, 46.1, and 48.9 °C (total 154 cans).

Statistical Treatments. Hicks' methods (1973) were used for calculation of linear and logarithmic regressions, and for analysis of variance (ANOVA) with orthogonal polynomials.

RESULTS AND DISCUSSION

Examination of 14 processed SSOJ samples (Table I) showed the following ranges of properties: pH (3.52–3.88), percent citric acid (0.77–1.11), total soluble solids (TSS) or degrees Brix (10.2–12.6), and degrees Brix/acid (10.6–16.1). Vitamin C values (as mg/6 fluid oz) were higher in early- (80.3–89.7) and mid- (89.4–104.8) season juices than in early-Valencia (71.2–86.3) and late-Valencia (55.4–73.0) juices. The vitamin C content of oranges and, therefore, processed orange juice is known to vary widely depending upon fruit variety, stage of maturity, climate, soil condition, geographic location, and other related factors (USDA, 1962). It has been reported the longer Valencia oranges remain on the tree, the greater will be the reduction of vitamin C (Harding et al., 1940). This was evident in our study also (Table I). Juice processed from late-Valencia oranges was lower in vitamin C than that from early-season Valencias. In fact, the juice from plant B (55.4 mg/6 fluid oz) did not meet the 100% U.S. RDA of vitamin C.

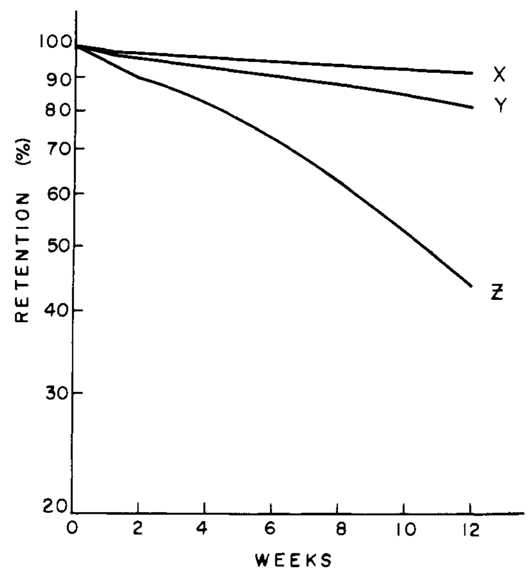

Figure 1. Percent vitamin C retention (logarithmic scale) vs. weeks of storage at 29.4 °C (X), 37.8 °C (Y), and 46.1 °C (Z).

We monitored juice from plant C (late-Valencia season) over a 12-week period to determine the mode of vitamin C degradation. Figure 1 shows the loss of vitamin C potency (log percent retention) during storage at 29.4, 37.8, and 46.1 °C. At all three temperatures, vitamin C decreased rapidly within the first 2 weeks. Such an initial rapid loss has been shown to be due to oxidation by a residual air layer trapped within the can during processing

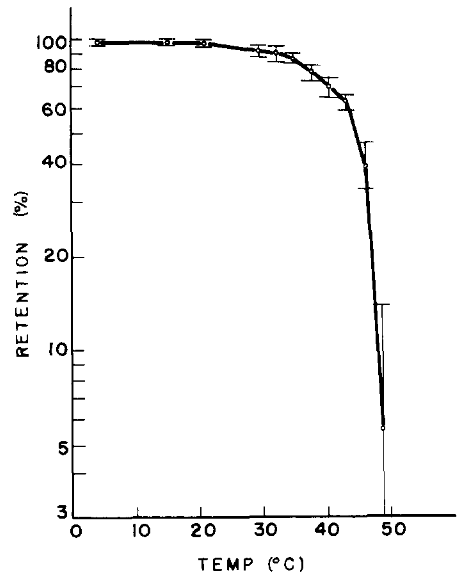

Figure 2. Percent vitamin C retention (logarithmic scale) vs. storage temperature for canned single-strength orange juice from 14 processing plants (mean and range shown).

(Kefford et al., 1959). After these initial 2 weeks, vitamin C was degraded anaerobically at rates specific but different for each temperature. The coefficients of determination (r^2) for the 29.4 °C-stored juice showed values of 0.98 and 0.97 for logarithmic and linear regression models, respectively. The r^2 values for 37.8 °C-stored juice were 0.94 (log) and 0.99 (linear) whereas those for 46.1 °C-stored juice were 0.93 (log) and 0.99 (linear).

Brenner et al. (1948) and Freed et al. (1949) studied the retention of vitamin C in canned SSOJ at 21.1, 32.2, and 37.8 °C. These workers concluded that the logarithm of vitamin C retention was linearly related to storage time at these three temperatures. No statistical treatment was applied to their data to confirm their interpretation. Figure 1 shows that although the relationship between log percent retention and storage time was linear for 29.4 °C, departure from this linear relationship (first-order reaction) was evident at 37.8 and 46.1 °C.

Empirically, a temperature rise of 10 °C usually increases the rate of most chemical reactions from 2 to 4 times. Over the 12-week period, the average rates of vitamin C loss (mg/100 ml of juice per week) were: 29.4 °C (0.28), 37.8 °C (0.63), and 46.1 °C (1.93). The rate of vitamin C loss increased ca. 2.3-fold from storage at 29.4 to 37.8 °C and increased ca. 3.1-fold between 37.8 and 46.1 °C. Thus, the rate of loss was disproportionally higher at the higher temperatures.

Because of the differential loss of vitamin C at the three storage temperatures, a study was conducted to determine the mode of vitamin C degradation over a wider temperature range (Figure 2). Retention of vitamin C between 4.4 and 21.1 °C was greater than 95%; however, average retentions from 29.4 to 48.9 °C ranged from 92 to 6%. Analysis of variance for the eight highest temperatures, i.e., from 29.4 to 48.9 °C, yielded the statistics shown in Table II. Within this temperature region, there were significant ($\alpha = 0.01$) linear, quadratic, cubic, quartic, and other unexplained higher order temperature effects. The orthogonal polynomial regression equation (Hicks, 1973) determined for this region was:

$$\bar{y} = 74.92 - 7.34\mu - 0.28\mu^2 - 0.41\mu^3 - 0.16\mu^4$$

where $\mu = (xj - 39.17)/2.8$, xj = temperature (degrees Celsius), and $\bar{y}$ = estimated vitamin C retention.

Table II. Analysis of Variance for Polynomial Model of Vitamin C Degradation[b]

Source	df	SS	MS	Fo
Between temp.	7	87 409.74		
T linear	1	73 144.01	73 144.01	7410.74[a]
T quadratic	1	12 363.09	12 363.09	1252.59[a]
T cubic	1	1 424.81	1 424.81	144.36[a]
T quartic	1	245.65	245.65	24.89[a]
T quintic	1	18.85	18.85	1.91
T higher orders	2	213.33	106.67	10.81[a]
Error	104	1 026.80	9.87	
Total	111	88 436.54		

[a] Indicates significance at the 1% level. [b] df, degrees of freedom; SS, sum of squares; MS, mean square; Fo, MS temperature order/MS error.

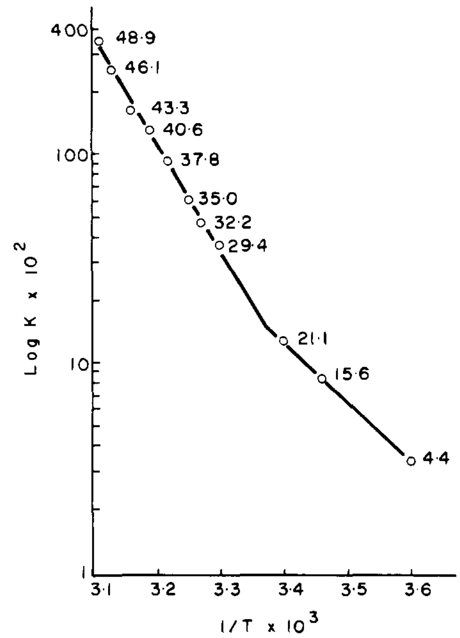

Figure 3. Arrhenius plot of log *K* (mg of vitamin C loss/100 ml of juice per week) vs. reciprocal of absolute storage temperature. Storage temperatures for the two Arrhenius profiles are also shown.

Early workers (Evenden and Marsh, 1948; Freed et al., 1949) studied vitamin C degradation in SSOJ and suggested that the rate of vitamin C loss obeyed the Arrhenius equation:

$$K = A\ \exp(-Ea/RT)$$

Thus, if log *K* were plotted vs. the reciprocal of absolute temperature, a straight line would be obtained. Figure 3 shows an Arrhenius plot of the log of the average rate constant (mg of vitamin C loss/100 ml of juice per week) vs. the reciprocal of absolute storage temperature. Within the storage temperature region, 4.4–48.9 °C, two distinct Arrhenius profiles are evident. One profile covers the lower temperature region of 4.4 to ca. 23.9 °C; the other, the higher temperature region of ca. 23.9 to 48.9 °C. The Arrhenius equation was obeyed within each of the two temperature regions but two different degradative pathways were indicated.

Recent interest in the nutritional value of food products has increased the need for information on factors which affect concentration of important nutrients. Temperature can affect vitamin C retention and, therefore, the level, as percent U.S. RDA of the vitamin in the citrus product. Processors could be charged with noncompliance if vitamin

Table III. Effects of High Temperatures on Percent U.S. RDA of Vitamin C in Canned Single-Strength Orange Juice after 12 Weeks Storage

		% U.S. RDA[a]								
Season	Plant	ZST[b]	29.4 °C	32.2 °C	35 °C	37.8 °C	40.6 °C	43.3 °C	46.1 °C	48.9 °C
Early	A	144	135	132	128	117	109	95	68	6
	B	134	125	122	114	107	97	89	58	2
	C	150	141	137	131	119	108	97	68	15
Mid	A	175	163	156	148	136	124	108	68	18
	B	149	136	132	127	116	103	92	59	22
	C	164	150	146	143	131	119	103	61	3
Early-Valencia	A	140	123	120	121	106	92	83	52	3
	B	119	112	108	105	95	86	77	50	3
	C	125	115	112	107	99	89	79	51	1
	D	144	131	130	127	114	101	92	59	14
Late-Valencia	A	115	100	96	96	84	74	75	38	9
	B	92	86	85	80	75	64	59	30	7
	C	122	112	110	106	96	81	75	39	3
	D	113	106	107	94	93	80	75	41	6

[a] 100% U.S. RDA equals 60 mg of vitamin C/6 fluid oz; metric equivalent for 100% U.S. RDA, i.e. 60 mg of vitamin C/177.4 ml. [b] Percent U.S. RDA of samples immediately taken from production lines after canning; zero storage time (ZST).

C contents of their products fall below the label-declared values (percent U.S. RDA).

At each specific temperature all 14 juices, regardless of plant or processing season, showed essentially similar percent vitamin C retentions. Since processed orange juice from all seasons shows fluctuations in vitamin C concentration, one critical factor in nutritional labeling will be the juice's initial concentration. This fact is readily demonstrated in Table III. This table shows the effects of temperature on percent U.S. RDA values in 14 juices stored 12 weeks at eight temperatures, viz. 29.4, 32.2, 35, 37.8, 40.6, 43.3, 46.1, and 48.9 °C. Juices with low initial levels of vitamin C could well have less than the 100% U.S. RDA value per serving after storage. Juices from the late-Valencia season are generally lower in vitamin C contents than juices from other seasons (Harding et al., 1940) and, therefore, would be most susceptible to fall below the 100% U.S. RDA level at high storage temperatures.

Many early investigators (Brenner et al., 1948; Evenden and Marsh, 1948; Joslyn and Miller, 1949; Huelin, 1953) assumed that vitamin C degradation in orange juice was a first-order reaction with the rate of degradation proportional to concentration. Thus, they believed that a linear relationship existed between vitamin C content (log percent retention) and time. Figure 1 shows that a nonlinear relationship exists between log percent vitamin C retention and time at high storage temperatures. Our data also showed that over a 12-week period loss of vitamin C more than doubled between 29.4 and 37.8 °C and more than tripled between 37.8 and 46.1 °C. Thus, as storage temperatures increased, there was a disproportionate loss of vitamin C.

The Arrhenius plot showed two distinct temperature regions. This plot indicated that storage of juices at temperatures higher than those of a critical region resulted in an accelerated rate of vitamin C breakdown. We estimate this critical transition region to be between 22 and 26.7 °C.

Employment of orthogonal polynomials in the analysis of variance (Table II) indicated that the mechanism of vitamin C degradation was not the same at all temperatures. Because of the nonlinearity between storage temperature and time, it is incorrect to assume that a mean storage temperature determined by averaging could be used for prediction of vitamin C retention in SSOJ stored at fluctuating warehouse temperatures over an extended period. Our results point out the need for cool storage facilities in preserving the nutritional quality of processed citrus juices, and indicate that short storage periods above 37.8 °C could be much more detrimental than predicted from rates of degradation at lower temperatures.

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