Investigation of the Color Changes in Heat Concentrated Tomato Pulp

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Pigment and color changes as a result of heat concentration of tomato pulp were investigated in juices reconstituted from pastes of 10, 15, and 20% soluble solids (10RJ, 15RJ, and 20RJ). With increasing heat treatment, the color measured by reflectance using a Hunter color difference meter

Upon processing, concentration, and storage of tomato products, many undesirable changes occur in the color, as well as in the flavor. Deterioration of the color of paste or tomato juice has been suggested to be caused by the browning products of the Maillard reaction by Luh *et al.* (1958a,b, 1964), Wong and Bohart (1957), and Danziger *et al.* (1970). However, by removal of the reducing sugars and amino acids responsible for browning, Cole and Kapur (1957) showed the color loss in heated serum-free tomato pulp to be the result of loss of lycopene, the carotene pigment responsible for most of the red tomato color. Montselise and Berk (1954) also have demonstrated the oxidative degradation of lycopene in tomato puree subjected to various heat treatments.

In this investigation, the changes in color and pigment content occurring in reconstituted tomato products as a result of heat concentration of tomato pulp were investigated.

EXPERIMENTAL SECTION

Sample Preparation. To provide tomato samples which had been treated with increasing amounts of heat, tomato pulp of 5% soluble solids (SS) was concentrated in individual batches in a vacuum evaporator at $46 \pm 1^{\circ}$ with a vacuum of 26 in Hg to pastes of 10, 15, and 20% SS. Within 24 hr the pastes were reconstituted to 5% SS and with the control or unconcentrated tomato pulp (I) thermally processed at 121° with a hold time of 42 sec, then filled in 6- and 9-oz glass jars as described previously (Gill and Noble, 1974). The juice samples were held at room temperature until analyzed.

Color Measurement. Color of the juice samples was measured by reflectance using the A head (large area of illumination) of a Hunter D25 color difference meter standardized against a white tile with the values L = 9.23, a = 0.7, and b = -0.9. Standard Agtron sample cups with plexiglass walls and glass bases (62 mm \times 38 mm) (Magnuson Engineering Corporation, San Jose, Calif.) were filled with juice to a level 5 mm from the top and the L, a, and b reflectance readings determined in triplicate.

Sensory Color Measurement. Samples were presented once to eight panelists in a random order in Agtron cups under illuminant C in an "Executive" Mac Beth-Munsell Color Hood. The panelists were asked to rank the samples from 1 to 4 in order of decreasing redness. Significance of results was determined from the rank sums (Kramer, 1960; Kramer *et al.*, 1974).

Pigment Determination. In preliminary work, browning was not shown to contribute to the color changes of the reconstituted juices. The hydroxymethylfurfural con-

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decreased in redness or hue, in saturation and in lightness. Total carotenoid content and isolated lycopene decreased with the heat concentration, resulting in losses of 11, 22, and 57% lycopene in the 10RJ, 15RJ, and 20RJ relative to the unconcentrated control tomato pulp.

tent of the sera of the samples, determined by the method of Luh *et al.* (1958a), was shown to decrease from 18 ppm in the control pulp to 12 ppm in the juice reconstituted from the 20% SS paste, and therefore only changes in the carotenoid pigment concentration were investigated.

Pigments determined in triplicate analysis were extracted by blending 5 g of juice in 100 ml of hexane for 4 min at low speed in a Waring Blendor. The xanthophylls were removed by rinsing the hexane extract with 95% and then 90% methanol rinses. The hexane extract was then diluted to volume and the absorbance read at 470 nm for spectrophotometric determination of the total carotene using a Bausch and Lomb Spectronic 20 spectrophotometer.

Lycopene was separated by column chromatography. The concentrated total carotene extract was applied to a column $(20 \times 200 \text{ mm})$ packed with 5 g of infusorial earth-magnesia (Fisher 2665, 1:1), and eluted under positive nitrogen pressure with 100 ml each of acetone-hexane (10:90), acetone-hexane (20:80), and acetone-hexane-methanol (20:79:1). The lycopene band which was eluted in the third solvent was diluted to volume and the absorbance read at 470 nm. Absorbance spectra of the lycopene collected from each juice sample were made in hexane between 350 and 520 nm using a Beckman Model DB recording spectrophotometer to verify the identity of the lycopene.

To prepare the standard curve of lycopene in hexane for spectrophotometric determination of the total carotenes as lycopene and of the isolated lycopene extracts, lycopene was isolated from 40 ml of tomato pulp as described above, rinsed with ethanol, dried, and weighed.

RESULTS AND DISCUSSION

The juices prepared by reconstituting the 10, 15, and 20% SS pastes (II, III, and IV) were characterized by perceptible color changes from the control pulp. Juice I, which received no heat concentration, was picked as the reddest sample by the panel and juice IV as the least red at the 5% level of significance (rank sums were I, 10; II, 17; III, 24; and IV, 29). The intermediate samples (II and III) had color differences which were not large enough for the panelists to reproducibly arrange the samples on the basis of decreasing redness.

By objective color measurement as shown in Table I, decreases in redness (measured as "a" or hue, "a/b") in saturation $[(a^2 + b^2)^{1/2}]$, and in lightness (L) occurred with the increasing amount of heat treatment. Similarly, in Table II, the total pigment (calculated as lycopene) and the actual lycopene content are shown to decrease upon heat treatment. Concentration to 10, 15, and 20% SS resulted in losses of 12, 20, and 36% of the total pigment and of 11, 22, and 57% of the lycopene, respectively.

The absorbance spectra of the isolated lycopenes compared well with the spectra of the prepared lycopene, used for the standard curve calibration, and with that reported

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Table I. Reflectance Measurements Using Hunter Color Difference Meter

	% SS of to- mato base	L (light- ness)	a (red- ness)	b (yellow- ness)	<i>a/b</i> (hue)	$\sqrt{a^2 + b^2}$ (satura- tion)
I	5	27.50	24.82	13.78	1.801	28.40
II Ш	10 16	$27.10 \\ 27.01$	$24.10 \\ 23.45$	$13.64 \\ 13.51$	$1.765 \\ 1.736$	$27.10 \\ 27.09$
IV	20	26.86	22.77	13.49	1.689	26.53

Table II. Determination of Pigment Concentration

Juice sample	Total carotenoids, ^{a,b} mg/g of juice	Lycopene, ^a mg/g of juice
1	0.050	0.037
II	0.044	0.033
III	0.040	0.029
IV	0.032	0.016
	1 1	

^a Calculated from absorbance at 470 nm. ^b Expressed as lycopene.

in hexane by Zechmeister (1962). The decrease in lycopene content reported here was due to an actual degradation of lycopene, rather than to a progressive conversion from the all-trans-lycopene to a less strongly colored, less intensely absorbing cis form. This was shown by the similar shape of log absorbance vs. wavelength curves for the lycopenes isolated from the control and reconstituted juices. As described by Zechmeister (1962) an increase in absorbance at 360 nm, producing dissimilar log absorbance curves, would have indicated trans-cis isomerization of lycopene.

The decrease in total pigment or isolated lycopene correlated with the decrease in redness (as measured by Hunter "a/b") at the 1% level of significance (r = 0.978and r = 0.907, respectively). This high correlation, with our preliminary evidence that in the sera browning (expressed as concentration of hydroxymethylfurfural) did not significantly occur upon paste concentration, suggests that the change in color, particularly in redness, of the juice products reconstituted from paste is a result of the degradation of the carotenoid pigments during the heat concentration of the paste. However, further investigation is needed to explain the darkening of the samples (as measured by decrease in "L") which occurs upon heat treatment.

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Isolation and Identification of Acidic Oligopeptides Occurring in a Flavor Potentiating Fraction from a Fish Protein Hydrolysate

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An enzymatic hydrolysate of a fish protein concentrate was fractionated to obtain a low molecular acidic fraction having a flavor potentiating activity. Almost 30 acidic oligopeptides were isolated from this fraction. By chemical and mass spectrometric methods, the complete or partial amino acid sequences of these oligopeptides were determined as follows: dipeptides, Ala-Glu, Asp-Ala, Asp-Gly, Asp-Leu, Glu-Asp, Glu-Glu, Glu-Gly, Glu-Ser, Ile-Asp, Ile-Glu, Ser-Asp, Thr-Glu, Val-Asp, and Val-Glu; tripeptides, Asp-Glu-Ser, Glu-Asp-Glu, Glu-Asp-Val, Glu-Gly-Ala, Glu-Gly-Ser, Glu-Gln-Glu, (Glu,Ile)-Asp, Ile-Glu-Glu, and Ser-Glu-Glu; tetrapeptides, (Asp,Glu,Gly)-Asp, (Asp,Glu,Ser)-Asp, (Asp,Gly,Ser)-Glu, and (Glu,Ile, Leu)-Glu; pentapeptides, (Asp,Glu,Gly, (Asp,Glu,Gly,Ser)-Glu, Ser)-Asp, and (Asp,Glu,Ser,Thr)-Glu; hexapeptide, (Asp,Glu₂, Gly,Ser)-Thr. Among these, peptides consisting of high molar ratios of glutamic acid residue were found to have a flavor activity qualitatively resembling that of monosodium glutamate.

Although most enzymatic hydrolysates of food proteins generally have a flavor potentiating activity like that of monosodium glutamate (MSG), these are often accompa-

nied by an unfavorable bitter flavor at the same time; factors responsible for the bitterness have been disclosed (Fujimaki et al., 1968; Matoba et al., 1969; Kirimura et al., 1969; Arai et al., 1970). Recently, several reports have been presented on peptides having a MSG-like flavor activity; these are hydrophilic glutamyl oligopeptides (Arai et al., 1972, 1973). In our preceding paper we have reported that a fish protein concentrate (FPC) treated with

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