FOOD FLAVORS INGREDIENTS AND COMPOSITION

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VOLATILE COMPONENTS AND FLAVOR OF PAPAYA (*Carica papaya* L.)

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SUMMARY

The volatile components of two papaya cultivars (Solo and Formosa) from the same geographic region (Bahia) and of the same cultivar (Solo) from two geographic regions (Bahia and Pará) were investigated. The cultivar Solo presented high percentage of linalool (up to 93%); with the exception of one sample, the second most abundant constituent was trans linalool oxide. The four lots analyzed for cultivar Formosa from the same geographic location showed great variability. This cultivar presented a greater proportion of the cis oxide, linalool being the second most abundant component. The esters methyl butanoate, crotonate and hexanoate varied markedly in their relative percentages, reaching in some chromatograms a very high relative proportion (up to 81, 97 and 21%, respectively). The quantitative descriptive analysis showed that the cultivar Solo had a more typical aroma with flower note and a more sweet flavor with nectar note. The cultivar Formosa presented an aroma with more green note and more bitter and watery flavor with green note. The cultivar Solo was preferred at 5% level of significance. The volatile composition of the cultivar Solo from Bahia and from Pará did not differ. The quantitative descriptive analysis also showed no significant difference in the aroma of Solo papayas from the two states. The flavor of Solo from Pará, however, was considered more sweet. Through the preference test, the untrained panel did not demonstrate preference for any one of the Solo papayas from different origin.

1. INTRODUCTION

Brazil's exports of tropical fruits, among them papaya, are on the rise. According to the Brazilian Association of Fruit Producers, Brazil with an exportation of only 5.3 million dollars in 1982, reached 18.5 million dollars in 1988, which signifies an increase in the order of 349% (1).

Domestically, papaya is a popular fruit, widely available all year round. It is part of the breakfast tables of hotels, restaurants and many homes. The cultivar Solo and Formosa are the most commercialized. The principal producing region is the

extreme South of the state of Bahia.

With its economic importance, more information about this fruit is needed. The carotenoid composition of Formosa and Solo papayas, along with two other cultivars, had been determined (2). The present study was conducted with the following objectives: (a) compare the volatile composition of the cultivars Solo and Formosa from Bahia; (b) verify sensory differences in aroma and flavor between the two cultivars; (c) compare the volatile composition of the papaya Solo from two geographic regions (North and Northeast); (d) verify corresponding differences in aroma and flavor.

The few studies dedicated to papaya volatiles (3-9) demonstrated great compositional variation, which had been attributed not only to cultivar differences and geographic effects but also to the treatment of the fruit samples before and during volatile concentration.

2. MATERIALS AND METHODS

2.1. Sample Preparation

The papaya samples were purchased from the Central market of Campinas. All samples were analyzed at the ripe stage. After quartering and manual removal of the peel and seeds of two opposite sections, the pulp was cut into 1 cm cubes and mixed immediately with 30% by weight of NaCl. Three hundred grams were placed in the sample flask of the simple trapping set-up (10). The headspace volatiles were swept to the Porapak Q trap (4 x 0.3 cm i.d., 60 mg Porapak Q) by suction. Trapping time for papaya volatiles was established to be 4 hours. The volatiles were desorbed with 300 ml pure hexane.

For the cultivar Formosa, 8 fruits taken at random from 4 lots of 15 fruits each were analyzed individually. For the cultivar Solo, 3 lots from each geographic location were sampled twice, each sample consisting of 3 fruits taken at random from a lot of 11 fruits.

2.2. Gas Chromatography

A Varian gas chromatograph model 3300 with flame ionization detector and integrator model 4290 was used to determine the relative percentages. The chromatographic conditions were: column, fused silica capillary column (50 m x 0.21 mm i.d.) of SE-54 (WCOT, SGE, USA); carrier gas, hydrogen at linear

velocity of 47 cm/s; make-up gas, nitrogen at 30 ml/min; detector temperature, 280°C; injector temperature, 250°C; injection technique, Grob splitless with hexane as solvent and splitless period of 0.75 min. The column temperature was held at 50°C for 8 minutes, programmed at 1.5°C/min up to 80°C, 3°C/min up to 130°C, 2°C/min up to 150°C and 5°C/min up to 230°C.

2.3. Identification of the Volatiles

The components were identified using a Shimadzu gas chromatograph model 14-A coupled with a mass spectrometer QP-2000. A fused silica capillary column (50 m x 0.21 mm i.d.) with the liquid phase OV-1 was used and temperature programming was carried out as described previously. Important operating parameters of the mass detector were: carrier gas, helium at 1 ml/min; detector temperature, 250°C; ionization voltage, 70 eV; scanning velocity, 1 scan s^{-1}.

Kovats indexes were also used as complementary parameters.

2.4. Sensory Evaluation

The fruits were cut into 2 cm cubes and evaluated in individual booths, under red illumination to mask color differences.

Eight descriptive terms for aroma and flavor were developed by 8 trained judges: flower, green, and typical for aroma and sweet, bitter, green, nectar and watery for flavor. Responses were recorded by 9 cm unstructured scales, anchored at the ends with the terms "none" and "strong", with 2 replicates.

Twenty judges also evaluated the samples, using 9 cm unstructured hedonic scales.

Additionally, the principal volatile components eluting from the chromatographic column were submitted to sniffing.

2.5. Statistical Analysis

The results of aroma and flavor sensory attributes were submitted to analysis of variance and principal component analysis. Data analysis was performed using SAS software (Statistical Analysis System).

3. RESULTS AND DISCUSSION

3.1. Volatile Composition

A total of 34 components were detected in the papaya cultivars, but only 10 appeared in appreciable amounts. Only these

principal compounds were identified.

The cultivar Formosa presented great variability not only between lots but also between samples of the same lot (Table 1). Except for one sample where methyl butanoate reached a relative percentage of 18%, the different samples of papaya Solo from Bahia had similar composition (Table 2). There was even better agreement between samples of the papaya Solo from Pará (Table 3).

TABLE 1
Relative percentages of the principal volatile components of papaya cultivar Formosa.

Volatile Compound	Relative percentage							
	Lot 1		Lot 2		Lot 3		Lot 4	
	1	2	1	2	1	2	1	2
methyl butanoate	tr	n.d.	74.0	81.0	1.3	0.2	n.d.	1.0
methyl crotonate	tr	n.d.	1.3	1.0	n.d.	n.d.	n.d.	97.4
methyl hexanoate	tr	n.d.	20.6	2.7	0.1	0.1	9.2	tr
methyl hex-2-enoate	n.d.	n.d.	0.5	0.2	n.d.	n.d.	n.d.	tr
cis linalool oxide	85.2	59.3	0.4	0.6	47.7	39.0	57.5	tr
trans linalool oxide	4.2	tr	n.d.	0.7	3.6	3.7	tr	n.d.
linalool	10.6	40.7	0.1	14.0	46.4	56.0	14.8	0.3
methyl octanoate	n.d.	n.d.	0.4	0.1	n.d.	n.d.	n.d.	n.d.
methyl geranate	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	n.d.
benzyl isothiocyanate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12.7	n.d.

tr = trace; n.d. = not detected.

TABLE 2
Relative percentages of the principal volatile components of papaya cultivar Solo from Bahia.

Volatile Compound	Relative percentage					
	Lot 1		Lot 2		Lot 3	
	1	2	1	2	1	2
methyl butanoate	tr	n.d.	tr	18.2	tr	tr
methyl crotonate	n.d.	n.d.	n.d.	0.5	tr	tr
methyl hexanoate	0.1	n.d.	0.2	0.4	tr	tr
methyl hex-2-enoate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
cis linalool oxide	1.8	3.6	2.4	2.3	3.0	3.0
trans linalool oxide	4.8	6.9	3.9	4.6	7.4	6.7
linalool	92.9	88.0	93.0	74.0	89.2	89.8
methyl octanoate	n.d.	tr	n.d.	n.d.	n.d.	tr
methyl geranate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
benzyl isothiocyanate	0.1	tr	0.2	n.d.	n.d.	n.d.

tr = trace; n.d. = not detected.

TABLE 3
Relative percentages of the principal volatile components of papaya cultivar Solo from Pará.

Volatile Compound	Relative percentage					
	Lot 1		Lot 2		Lot 3	
	1	2	1	2	1	2
methyl butanoate	tr	n.d.	n.d.	n.d.	n.d.	n.d.
methyl crotonate	tr	n.d.	n.d.	n.d.	n.d.	n.d.
methyl hexanoate	0.1	tr	0.1	0.1	tr	tr
methyl hex-2-enoate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
cis linalool oxide	2.5	4.5	4.2	3.0	4.0	5.0
trans linalool oxide	4.9	6.2	4.5	4.2	6.6	3.8
linalool	92.4	89.3	90.8	92.6	89.2	90.6
methyl octanoate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
methyl geranate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
benzyl isothiocyanate	0.1	n.d.	0.2	0.1	tr	0.6

tr = trace; n.d. = not detected.

In spite of the variation encountered in the cultivar Formosa, marked differences could be observed between the two cultivars. In the papaya Formosa, with the exception of one chromatogram, the cis oxide exceeded the trans oxide of linalool and was the major component in four samples from three lots with relative percentages of 85, 60, 48 and 58%. In these samples, linalool was the second principal volatile with percentages of 11, 41, 46 and 56%. In the two samples of lot 2, methyl butanoate predominated with 74 and 81%; the second major component was methyl hexanoate (21%) in one sample and linalool (14%) in the other sample. One sample of lot 3 had linalool as the main component, followed by the cis-oxide. In one sample of the fourth lot, methyl crotonate reached 97%. The occasional high percentages of methyl butanoate, methyl crotonate and methyl hexanoate were not observed in the cultivar Solo. The highest percentage of butanoate obtained in this cultivar was 18% found in only one sample. The cultivar Solo was characterized by the predominance of linalool, which was always the major component, with relative percentage of up to 93%. The second principal component was trans linalool oxide.

Excluding two samples, one with 18% of butanoate (Solo from Bahia) and another with the cis oxide greater than the trans oxide of linalool (Solo from Pará), 10 samples (five for each geographic origin) presented similar composition, thus showing no geographic effects.

3.2. Sensory Analysis

The cultivar Solo had a more typical and flower aroma and more sweet and nectar flavor. The cultivar Formosa presented an aroma with more green note and more bitter, watery and green flavor (Table 4). This can be seen better in Figure 1, where the distance from the origin to the end of the scales represents the average intensity scores ascribed to eight attributes for the three samples. There is no significant difference in the aroma of Solo papaya from two different states; however, the flavor of Solo from Pará was considered more sweet.

TABLE 4

Mean scores for sensory attributes of papaya[1].

Sensory Attribute	Samples		
	Solo-Pará	Solo-Bahia	Formosa
AROMA			
flower	4.29a	4.14a	0.72b
typical	3.62a	3.62a	2.42b
green	0.95b	0.45b	2.54a
FLAVOR			
sweet	6.20a	2.60b	1.00c
bitter	0.00b	0.40b	1.10a
green	0.10b	0.50ab	1.10a
nectar	3.90a	2.50a	0.60b
watery	0.10c	2.00b	4.50a

[1]Mean values of eight panelists with two replications (16 values) Within an attribute, means sharing the same postscript do not differ at $p<0.05$.

The principal component analysis showed that for both aroma and flavor, the samples most separated from the others were those of the cultivar Formosa (Figures 2 and 3). For aroma this cultivar was located at the left for the principal component 1, where the attribute green points. For flavor the cultivar Formosa samples were located at the right hand of the principal component 1, where the attributes green, watery and bitter point.

The results of the preference test were coherent with those of the quantitative descriptive analysis. The averages obtained were 7.24, 6.71 and 3.42 for Solo from Bahia, Solo from Pará and Formosa, respectively, the latter being significantly lower ($p<0.05$).

Considering the volatile component and sensory (aroma)

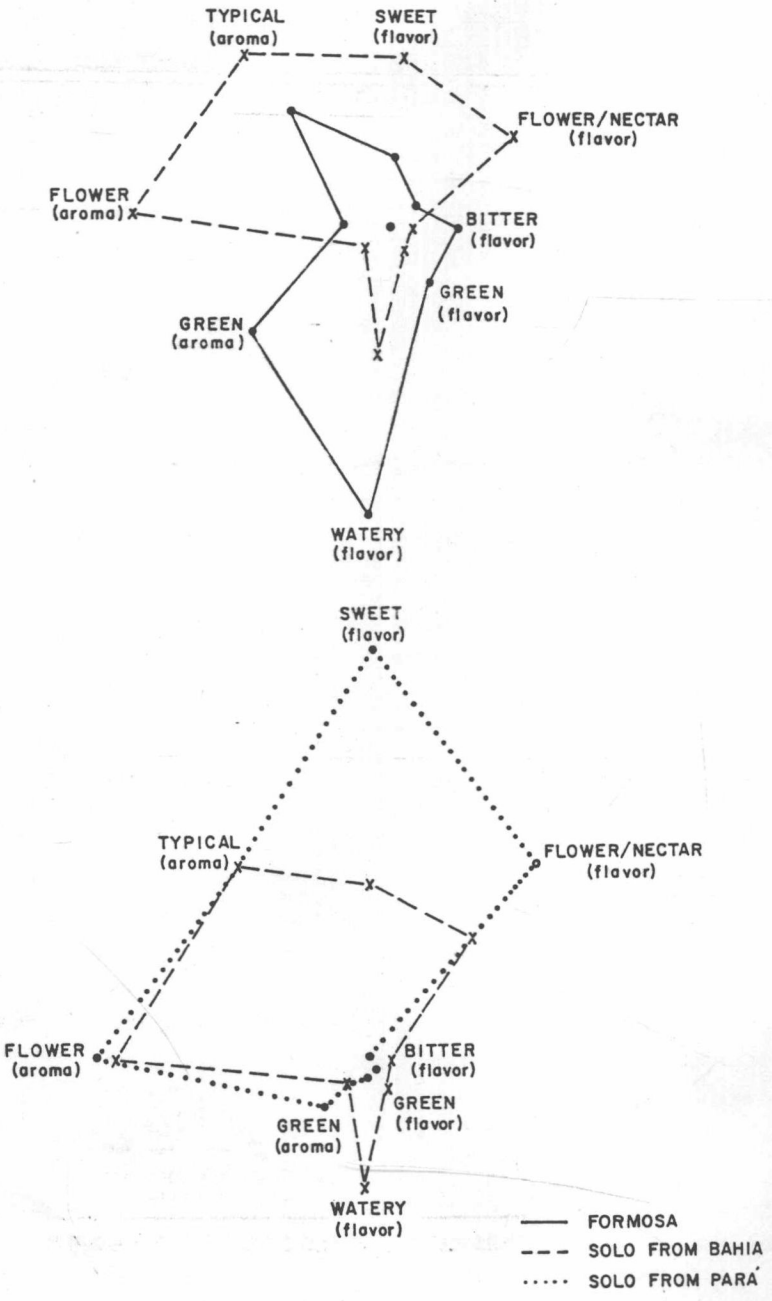

Figure 1 - Comparative descriptive profile of aroma and flavor of two cultivars of papaya.

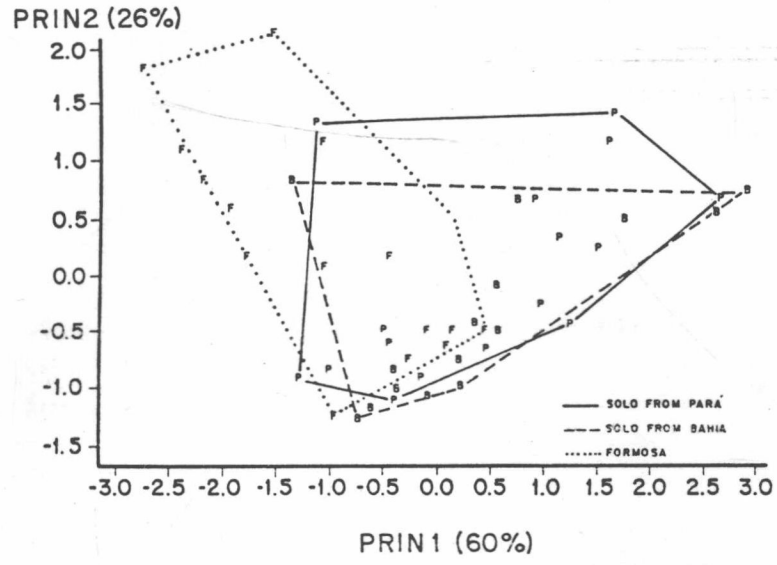

Figure 2 - Principal component analysis for aroma of papaya.

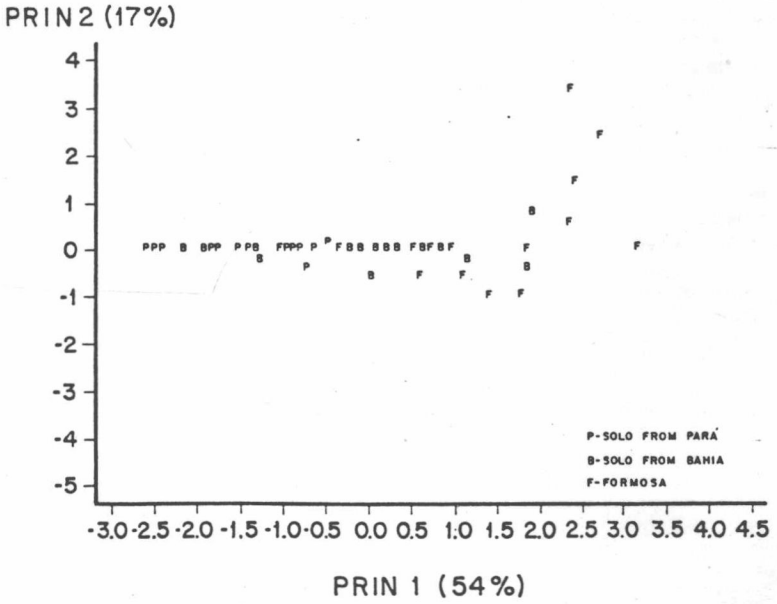

Figure 3- Principal component analysis for flavor of papaya.

results together, no difference was observed between papayas of the cultivar Solo from Bahia and Pará. The cultivar Solo, which was preferred over the cultivar Formosa, showed predominance of linalool, a compound described as flower, yasmin or perfume by sniffing. The sensory evaluation attributed typical and flower aroma and nectar flavor to this cultivar.

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G. Charalambous (Ed.), Food Flavors, Ingredients and Composition

Relationship between sulphur dioxide level and inhibition of browning in apricots dried to different moisture levels

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Abstract

The relationship between the extent of browning development and residual SO_2 level in dried apricots following different pretreatments was studied. Assessment of the degree of browning by optical density and Hunter L and b measurements indicated the moisture content to be a major determinant of the interrelation between residual SO_2 and inhibition of browning. The desired colours were availed at lower levels of residual SO_2 in apricots with relatively higher moisture contents. Ascorbic acid appeared to protect the yellowness, but not lightness or brightness in low-moisture dried apricots. Extension of dipping time actually increased the level of residual SO_2 necessary for inhibition of browning.

1. INTRODUCTION

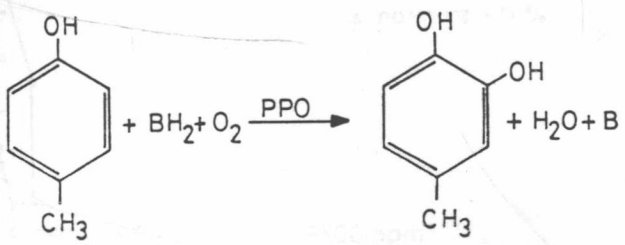
The apricot (*Prunus armeniaca*) is a popular and nutritious fruit having a high level of ß-carotene and a large potassium to sodium ratio. It is grown extensively throughout Eastern Anatolia, especially in the Malatya Province, and about 95% of the produce is exported. The harvesting season, although subject to yearly variation according to the weather conditions, is generally between the 1st and 3rd week of July.

Drying is one of the most common methods of preserving apricots and other perishable fruits with short harvesting seasons. Apricots produced in Turkey are traditionally sun-dried and are usually exported as the dried fruit. However, the combined effects of climatic factors and shortcomings in the sun-drying technique can often result in a poor quality product. Hence, there are many potential difficulties to be recognized and overcome before the apricots can successfully be marketed both domestically and internationally. Since poor quality produce represents an economic loss and can be hazardous to health, the contributions to the final product of the processing conditions, quality of the raw materials, and additives used during processing need to be carefully assessed and understood. In this context, improvement of pre-drying operations are specially important to the marketability of apricots.

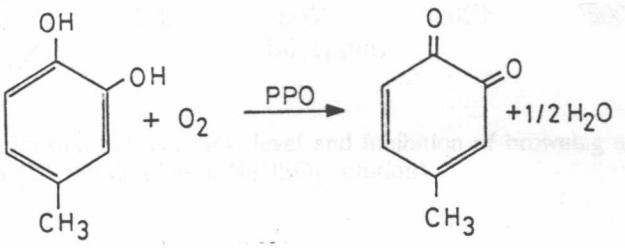
Browning during the drying of apricots, which is essentially enzymatic in origin, is a major cause of quality loss. It is caused by the induction of structural changes in phenolic compounds (mainly catechins) by the enzyme polyphenol oxidase (PPO).

PPO is a copper-containing enzyme which catalyzes two different reactions in the presence of molecular oxygen [1, 2]:

a. The hydroxylation of monophenols with a para substituted methyl or methylene group to the corresponding o-dihydroxy compounds



b. the oxidation of o-dihydroxy phenols to o-quinones



The quinones thus formed then undergo secondary polymerization reactions yielding dark, insoluble polymers which are responsible for the browning of the dried fruit. The o-quinones form macromolecular complexes with amino acids or proteins reducing their digestibility and the availability of lysine. o-Quinones also oxidize compounds of lower oxidation-reduction potentials, thus providing fresh substrate to the oxidative action of the enzyme. Ascorbic acid inhibits this reaction while being depleted itself by PPO. Therefore, the occurrence of enzymatic browning indicates total loss of vitamin C [3, 4].

The degree of browning depends on the concentration of the phenolic substrate and the localization of the substrate and enzyme in the plant. PPO is usually inactivated at temperatures above 70° C; however, the enzyme in apricots is relatively temperature stable and the efficiency of thermal treatment depends on pH (unstable at pH < 3 and most stable at pH 5) [3]. The problem of enzymatic browning in fruits is commonly resolved by heat inactivation, exclusion of substrates, sulphite addition, and ascorbic acid addition [5-7]. The first two of the methods cited may be effective in retarding browning, but are not practical for the drying of apricots.

Sulphur dioxide application is the most common and possibly the only commercially applicable method for the prevention of enzymatic browning in apricots. It has the unique property of retarding both enzymatic and nonenzymatic browning, and of providing antimicrobial protection at a low concentration [8]. Traditionally in Turkey, apricots are sulphured in a room where elemental sulphur is burned in the presence of oxygen to produce sulphur dioxide gas.

The internationally accepted level of sulphur dioxide in apricots is 2000 ppm maximum. However, concern over the danger of asthma induced in people susceptable to sulphites and the increasing market demand for foods devoid of added chemicals

have created a need for lower residual levels of SO_2 [9, 10]. On the other hand, the minimum level of SO_2 necessary to prevent browning and ensure stability during storage of Turkish apricots was not known. As dried apricots are one of the major Turkish export products, it is particularly important to lower their SO_2 levels to the bare minimum necessary to maintain quality without impairing their marketability.

This work was undertaken to study the effect of high and low-moisture drying, with and without ascorbic acid pretreatment, on the relationship between sulphur dioxide level and the inhibition of browning in apricots grown in Turkey.

2. MATERIALS AND METHOD

2.1. Materials

Fresh apricots (var. Mut) from Southern Anatolia were obtained from a wholesale fruit market and kept at 3-4° C until use within 2 weeks of purchase.

2.2. Methods

Fresh apricots taken from the storage room were immediately washed, cut in half to remove the pits and allotted into two groups. The apricots in the first group were dipped in $NaHSO_3$ solutions of increasing concentrations (0.5-25%) for 20 min to achieve levels of SO_2 in the appropriate range. The apricots in the second group were dipped in $NaHSO_3$ solutions of the same concentrations containing 0.1% ascorbic acid for 20 min. The apricots in each group were then separated into 2 sub-groups which were dried in an oven at a temperature of 60° C to two different moisture levels (11% and 33-34%). A trial was also conducted with fresh apricots dipped in $NaHSO_3$ and $NaHSO_3$+0.1% ascorbic acid solutions for 1 h. In this trial, apricots were dried to the lower moisture levels (10-13%) only.

Moisture was determined by the AOAC Method No. 22.013 [11] and the residual sulphite in dried apricots by the Modified Monier-Williams method (AOAC Methods No. 20.123- 20.125) [12]. Colour (L and b values) was measured using a Model D 25 A-9 Hunterlab tristimulus colorimeter. Optical density was measured in a Milton Roy 1201 Model spectrophotometer on samples prepared according to the method of Abdel-haq and Labuza [13]. A value of optical density below 0.10 was considered satisfactory by these workers and was also adopted as the acceptable range in the present work. Apricots with values of L and b above 40 and 20 respectively were considered to be acceptable with regard to brightness and yellowness as evaluated by comparison with commercially marketed products.

3. RESULTS AND DISCUSSION

The relationships between SO_2 level and inhibition of browning in dried apricots pretreated with $NaHSO_3$ solutions for 20 min are plotted in Figures 1-3 with respect to absorbance at 440 nm, Hunter L (brightness) values, and Hunter b (yellowness) values. These three parameters are indicators of sensory properties that are of crucial importance to the marketability of dried apricots.

The desired inhibition of browning as depicted by absorbance at 440 nm ($\leq$0.10) [13] was obtained at the SO_2 level of 6600 ppm in apricots with the lower moisture level (11%), whereas the same inhibition was attained at an SO_2 level of 550 ppm in apricots with the higher moisture content (33-34%). The same trend, although slightly less pronounced, was observed with respect to Hunter L and b measurements.

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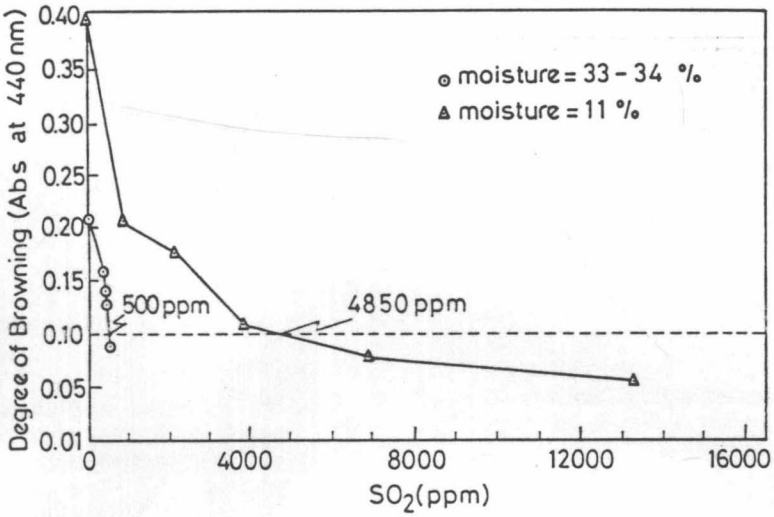

Figure 4. Relationship between SO_2 level and inhibition of browning at two different moisture levels (20 min dipping in $NaHSO_3$ + 0.1% ascorbic acid solution)

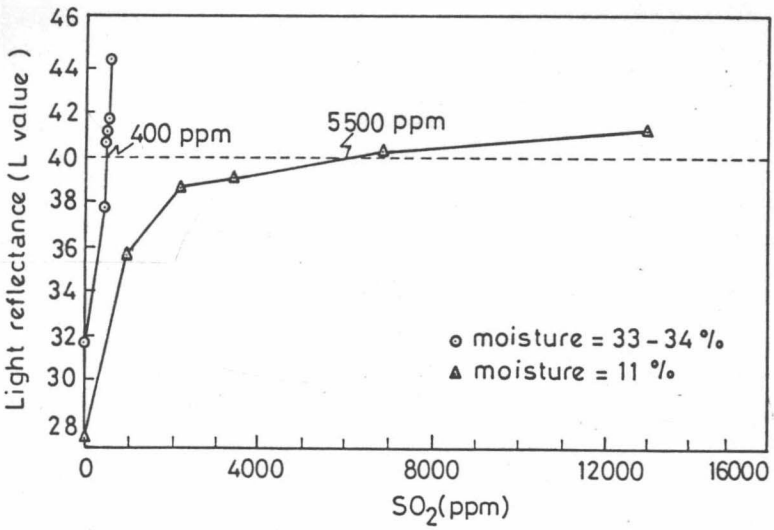

Figure 5. Relationship between L (Hunterlab) value and SO_2 level at two different moisture levels (20 min dipping in $NaHSO_3$ + 0.1% ascorbic acid)