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CHEMICAL CHANGES IN UNPASTEURIZED AND PASTEURIZED BALADI AND VALENCIA ORANGE JUICES DURING COLD STORAGE

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ABSTRACT: Thermal processing used in orange juice production is designed to inactivate contaminating microorganisms, pectinesterase and other undesirable enzymes, but it can alter the physical and chemical properties of the juice. The changes in chemical constituents of orange juices prepared from Baladi and Valencia oranges due to pasteurization and storage at 8°C were investigated.

Freshly-squeezed unpasteurized Baladi orange juice was characterized by 11.5° Brix total soluble solids (TSS), 1.28% titratable acidity, 5.22% reducing sugars, 3.86% non-reducing sugars, 57.8 mg/100 ml vitamin C, 8.4 mg/100 ml free amino nitrogen and 1.8 mg/L carotenoids. The respective values found in Valencia orange juice were 11.3, 0.93, 3.96, 4.52, 60.4, 8.4 and 8.90.

Pasteurization reduced the contents of vitamin C and carotenoids, while the contents of TSS and titratable acidity were increased. The concentrations of reducing and non-reducing sugars remained unchanged. Remarkable increase in browning index of juices after pasteurization was observed. Storage at 8°C showed pronounced decrease in TSS, vitamin C, free amino nitrogen and carotenoids, whereas titratable acidity was increased.

It can be concluded that, thermal pasteurization alter the chemical characteristics of orange juice and alternative cold pasteurization such as high pressure processing must be employed to preserve the nutritional and quality attributes of the fresh unpasteurized juice.

INTRODUCTION

Orange juice has been produced in several forms such as frozen concentrate, orange juice from concentrate, orange juice not from concentrate and pasteurized juice. Although, these products must conform to strict standards which prevent unnatural changes, recent awareness for diet and nutrition has directed the consumers to demand more natural products. Thermal processing used in orange juice production is designed to inactivate contaminating micro-organisms, pectinesterase and other undesirable enzymes systems. However, this heat treatment (pasteurization) can cause changes in physical and chemical properties of the juice (El-Hashimy, et al. 1980 and Farnworth et al., 2001), it drives off volatiles influencing orange juice flavor and alters the nutritional qualities. On the other hand, pasteurized orange juice not from concentrate (NFC) is superior in taste to reconstituted juices (Shaw et al., 1993). The manufacture of refrigerated unpasteurized orange juice has become more common and achieved consumer satisfaction. According to Information Resource Inc. data, the total $ sales of chilled orange juice and specially blends in USA is 2.5 million $ (Katz and Gies, 1998).

Based on subjective flavor evaluations, it has been reported (Fellers, 1988) that shelf life of refrigerated unpasteurized orange juice is relatively short. Therefore, maintenance of high sanitation and low temperature (-1 to 0°C) throughout the production and storage is requisite to extend shelf life for longer period.

The Egyptian fruit juice and fruit drink market is expanding sharply last few years. Most of these juices are pasteurized and prepared from concentrates. The increased consumer awareness towards having healthy and nutritional foods, will surely direct the juice producers to develop more fresh and minimally heat treated products. At the present time, limited quantity of fresh squeezed-unpasteurized orange juice is produced only in hyper supermarkets, but not at a commercial scale.

The aim of the present study was to evaluate the chemical characteristics of freshly squeezed-unpasteurized orange juice and pasteurized juices prepared from Baladi and Valencia oranges during storage at 8°C.

MATERIALS AND METHODS

Orange fruits (*Citrus Sienensis var.Baladi*) were harvested from Hehya district in El-Sharkia Governorate, Egypt, at full maturity at 2000-2001 season. The harvesting dates were December and January. Valencia orange fruits were purchased in May (2001) from Zagazig local market.

Orange fruits were washed with chlorinated tap water (9 ppm chlorine), rinsed with tap water and allowed to drain. The fruits were cut into two halves and extracted by laboratory hand reaming. The juice was strained through two layers of cheese cloth.

Total solids of freshly extracted Baladi orange juice was 12.4° Brix, and of *Valencia orange juice* was 11.6° Brix. The yield of Baladi juice was 48.5%, but of Valencia orange juice was 51%. For the preparation of non-pasteurized orange juice, the freshly squeezed juice was packed in sterilized glass bottles (250 ml), caped and kept at 8°C. For the preparation of pasteurized orange juice, the juice was preheated in stainless steel pot to 80°C, then filled in sterilized glass bottles (250 ml) caped and put in water-bath to 90°C for 10 min. The bottles were cooled directly using tap water and stored at 8°C. Total soluble solids were determined using refractometer (Atago, Japan) at 20°C. Titratable acidity was measured by titrating 10 ml juice with 0.1 N NaOH using phenolphthaline as indicator. pH value was determined using pH meter Model (41150 S/N 970aa 411 ICM 163 S.W). Freeman. Free amino nitrogen was determined using formol volumetric titration method A.O.A.C. (2000). Ascorbic acid was determined using 2,6 dichlorophenol indophenol A.O.A.C. (2000). Browning index was determined by using 85% acetone as a solvent. Reducing, non-reducing and total sugars contents were colorimetrically determined according to the method of Bernfeld (1955). Carotenoids content was determined according to the method described by Wettestein (1957) using acetone 85% as a solvent. The color was measured at 440 nm, 644 nm and 662 nm. The following equations were used to calculate the carotenoids:

Chlorophyl a = (9.784xE662)-(0.99 x E 644) = mg/L.

Chlorophyl b = (21.426 x E 644)-(4.65 x E 662) = mg/L.

Carotenoids = (4.495 x E 440)-0.268(chl. a + chl. b)= mg/L.

Where: E is the absorbance at the indicated wavelength.

RESULTS AND DISCUSSION

1. Total soluble solids (TSS):

Fig. 1 shows the total soluble solids content of unpasteurized and pasteurized orange juices prepared from Baladi and Valencia oranges. Freshly squeezed Valencia and Baladi juices contained similar total soluble solids content accounting for 11.5 and 11.3° Brix, respectively. On pasteurization, the TSS increased by 11.50 and 16.81 %, respectively. This is probably due to solubilization of water soluble components from the pulp particles as a result of heat treatment used in pasteurization. This result agrees with those obtained recently by Farnworth et al. (2001) who found that TSS contents of unpasteurized and pasteurized Mexican orange juices were 11.6 and 12.1° Brix. Storage of unpasteurized and pasteurized juices at 8°C resulted in marked decline in TSS content. The reduction in TSS content during storage was faster in unpasteurized Baladi orange juice than in Valencia orange juices. Moreover, pasteurization process resulted in higher reduction in TSS content during storage The loss in TSS during storage can be ascribed to the involvement sugars, nitrogenous compounds and ascorbic acid in browning reactions.

2. Titratable acidity:

Fig. 2 shows titrable acidity (expressed as % anhydrous citric acid) of orange juice extracted from Baladi and Valencia oranges. Unpasteurized Baladi orange juice contained remarkably higher acid content (1.28%) than unpasteurized Valencia orange juice (0.93%). The variability of acid content in different orange juices is due to variety of the fruit used, and the *stage of maturity*. *Fellers (1988)* found that, total acid content of freshly squeezed unpasteurized orange juice extracted from early Valencia, Hamlin, pineapple orange and late Valencia were 1.02, 0.77, 0.70 and 0.65%, respectively. These data indicate that Baladi oranges produce juice which is characterized by the highest acid content as compared to *juices extracted from several* orange varieties. The wide difference in acidity between Baladi and Valencia orange juices can be explained on the basis of compensation point temperature which varies from fruit to fruit as well as growing conditions (Kimball, 1991). At this point, the photosynthesis and respiration are

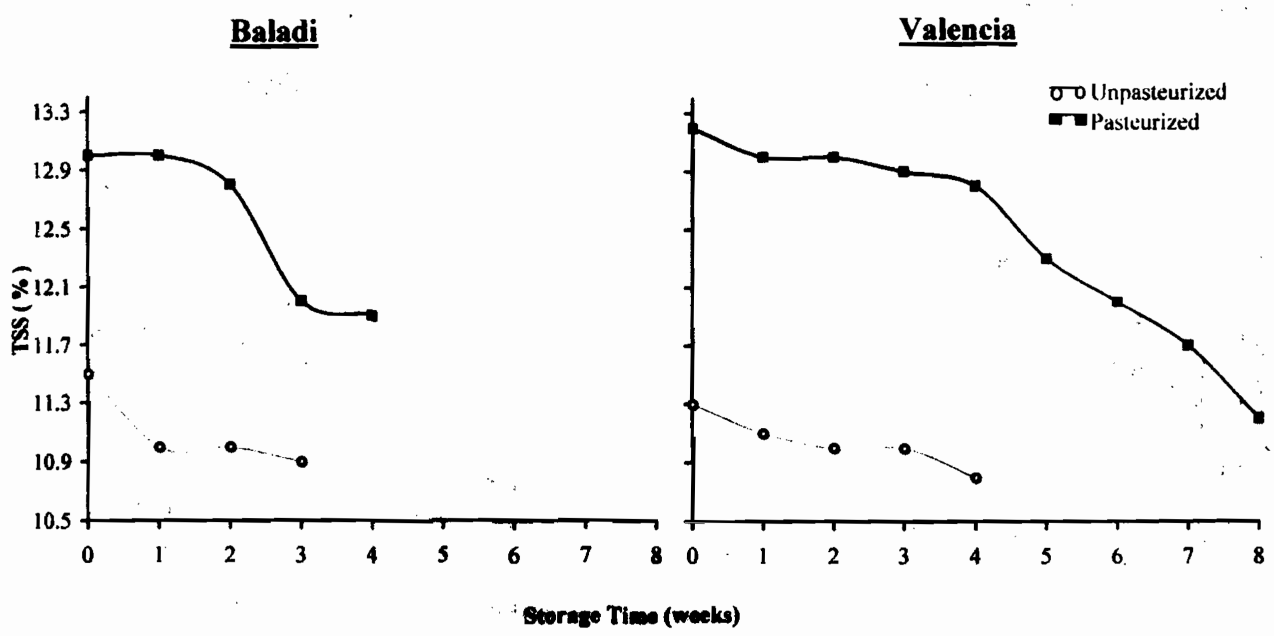

Fig. 1: Effect of pasteurization and cold storage on TSS of Baladi and Valencia orange juices.

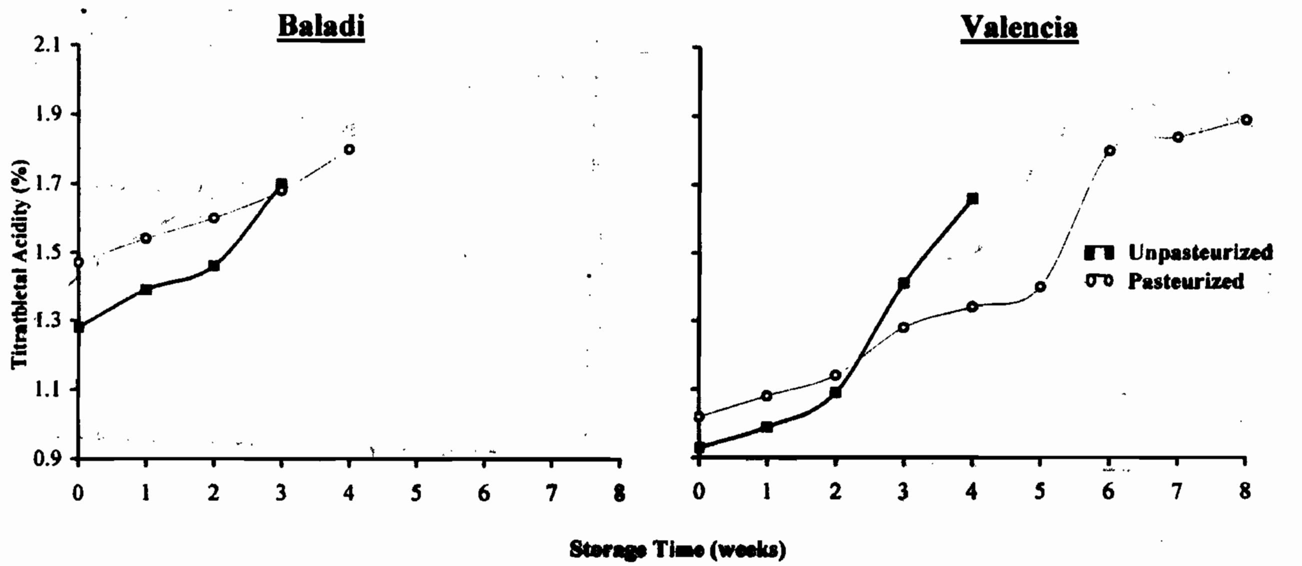

Fig. 2: Effect of pasteurization and cold storage on titratable acidity of Baladi and Valencia orange juices.

equal. At temperature above the compensation point, the fruit will draw on not only the carbohydrate reserve, but the citric acid reserve found in the juice cell vacuoles, causing a drop in citric acid levels; such drop of acid level is common with Valencia oranges. On the other hand, Baladi fruits which ripen in winter never exhibit the same sharp drop in acid level, but follow smooth change in acid concentration. Pasteurization caused elevation in the acid concentration compared to unpasteurized juice. This effect is a result of solubilizing acidic components from the pulp particles due to heat of pasteurization. Similar findings have been reported by El-Hashimy (1980). The first 2 weeks of storage of unpasteurized orange juice reflected an increase in titratable acidity after that sharp increase was observed. The increase in titratable acidity of unpasteurized orange juices may be due to microbial contamination. Pasteurized orange juice samples showed also gradual increase throughout the storage period.

3. Sugars:

Figs. 3, 4 and 5 present reducing, non-reducing and total sugars contents of Baladi and Valencia orange juices, both unpasteurized and pasteurized during cold storage. Reducing sugars in orange juices are mainly glucose and fructose which are present in orange juice in a ratio 1:1 (Voldrich et al., 2002). Baladi orange juice is characterized by higher reducing sugars content (5.22%) than Valencia orange juice (3.96%). These results are in accordance with those reported by Min-Kyoung, et al. (1997) for Baladi orange juice and Lanza (1984) for Valencia orange juice. Pasteurization process did not affect the concentration of reducing sugars in Baladi and Valencia orange juices. Moreover, storage of unpasteurized juices at 8°C did not significantly affect the concentration of reducing sugars. Results obtained by Babsky (1986) are in accordance with the results obtained in the present study. Similarly, non-reducing sugars did not show significant change during storage of unpasteurized and pasteurized orange juices prepared from Baladi or from Valencia oranges. From results presented on the concentration of reducing and non-reducing sugars in Baladi and Valencia juices, it is evident that one can differentiate between both types of juices on the basis of their sugars contents. Baladi orange juice is characterized by higher reducing sugars and lower non-

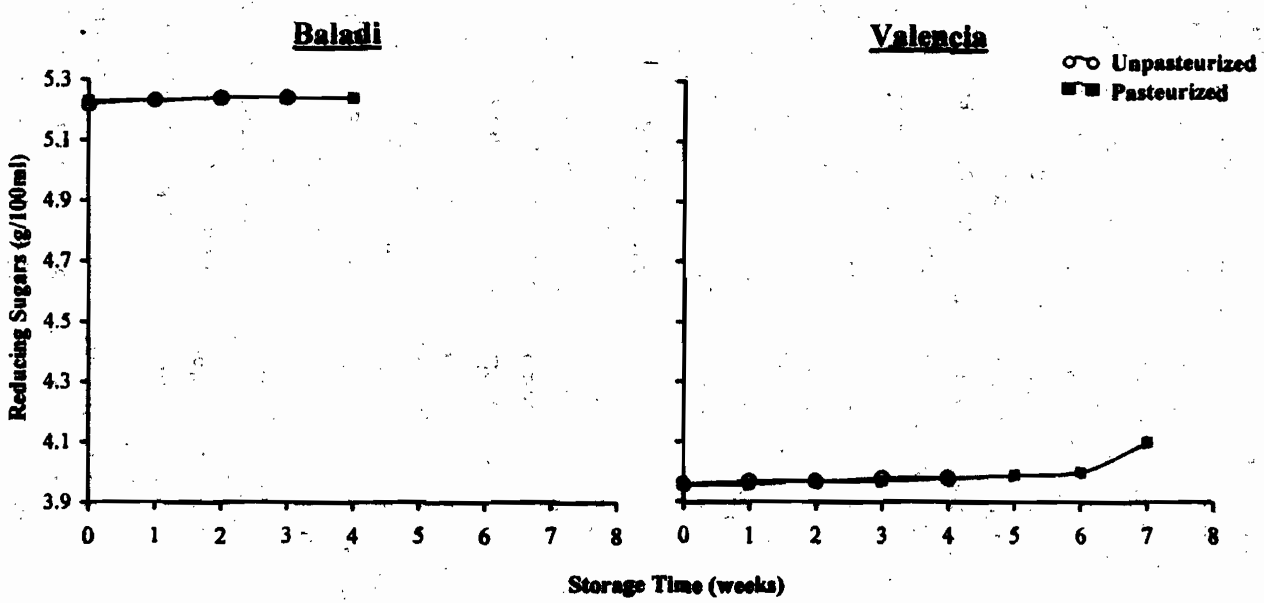

Fig. 3: Effect of pasteurization and cold storage on reducing sugars of Baladi and Valencia orange juices.

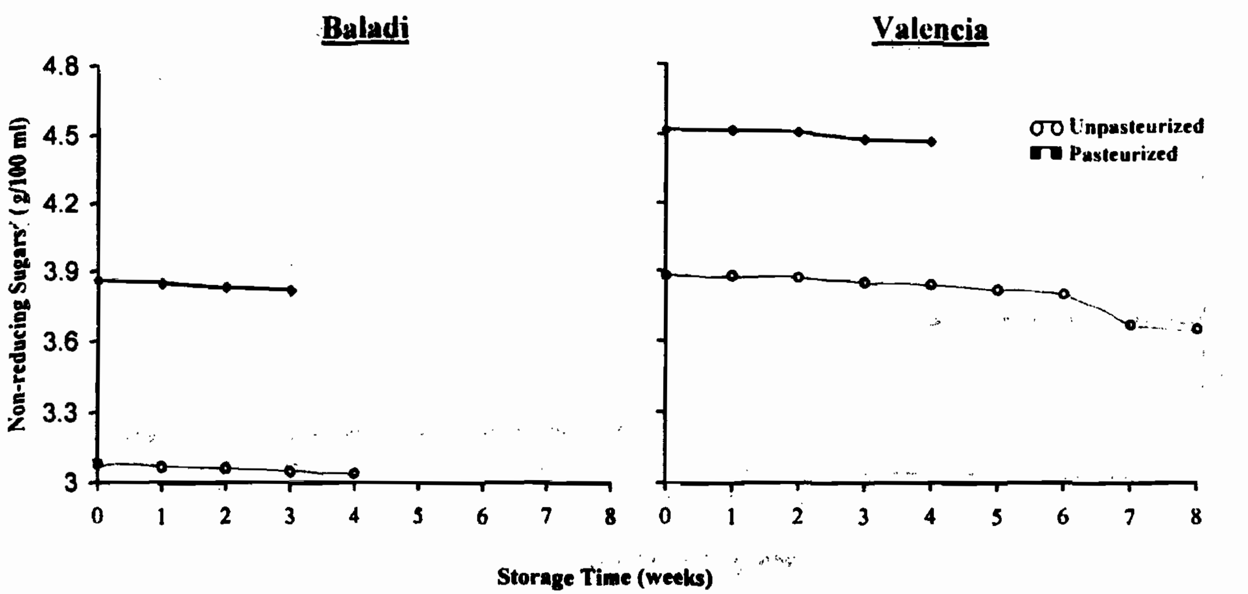

Fig. 4: Effect of pasteurization and cold storage on non-reducing sugars of Baladi and Valencia orange juices.

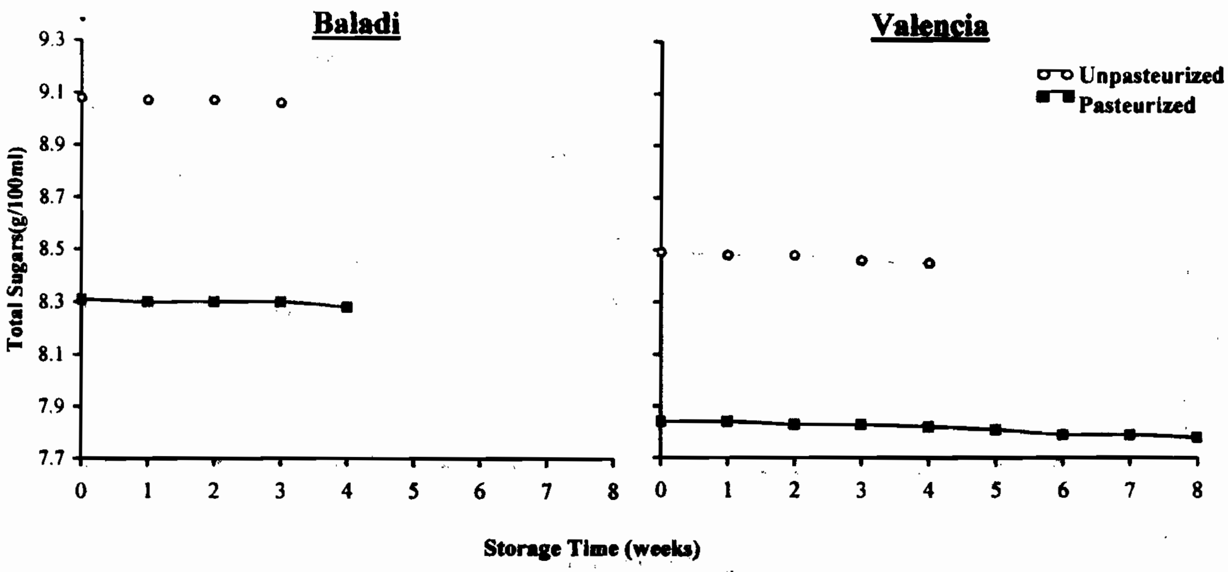

Fig. 5: Effect of pasteurization and cold storage on total sugars of Baladi and Valencia orange juices.

reducing sugars content compared to Valencia orange juice (Figs.3 and 4).

Pasteurization resulted in a reduction in non-reducing sugars in both types of juices. Farnworth (2001) reported that, pasteurized Mexican orange juice exhibited significantly larger sucrose and fructose concentrations compared to unpasteurized juice which contradicts with data obtained in the present study.

Total sugars content of Baladi orange juice was found to be higher than that found in Valencia orange juice. The sum of sucrose, glucose and fructose (9.15%, w/v) reported by Farnworth (2001) compares favorably with total sugars content found in the present study. Pasteurization did not show pronounced changes in the concentration of total sugars contents.

4. Vitamin C:

Orange juice has long been known to be an excellent source of vitamin C. Fig. 6 shows that higher vitamin C content was found in unpasteurized Valencia orange juice (60.4 mg/100 ml) than unpasteurized Baladi orange juice (57.8 mg/100 ml). These values agree with those reported by several authors for fresh orange juice (Nagy, 1980; Fellers, 1988 and Farnworth et al., 2001). Moreover, it has been documented that, early and mid- season fruit (primarily, Hamlin and Pineapple oranges) processed into chilled juices between January and April consistently showed higher levels of vitamin C than fruit (primarily Valencia oranges) processed during the late season, April to July (Nagy and Smoot, 1977 and Nagy, 1980).

Pasteurization significantly affected the concentration of vitamin C. The loss of vitamin C in Baladi orange juice due to pasteurization was found to be 11.76%, while the respective value for Valencia orange juice was 13.44%. El-Hashimy, et al. (1980) indicated that pasteurization process reduced vitamin C concentration of orange juice. Moreover, vitamin C concentration was markedly decreased during storage of Baladi and Valencia orange juices. Destruction of vitamin C in foods takes place in two ways: enzymatic destruction by several enzymes systems such as cytochrome oxidase, ascorbic acid oxidase and peroxidase. The second way of destruction is of non-enzymatic nature occurring through aerobic and non-aerobic reductions. The incorporation of air into the juice during extraction, finishing and filling has been recognized as causing vitamin C loss (Lee and

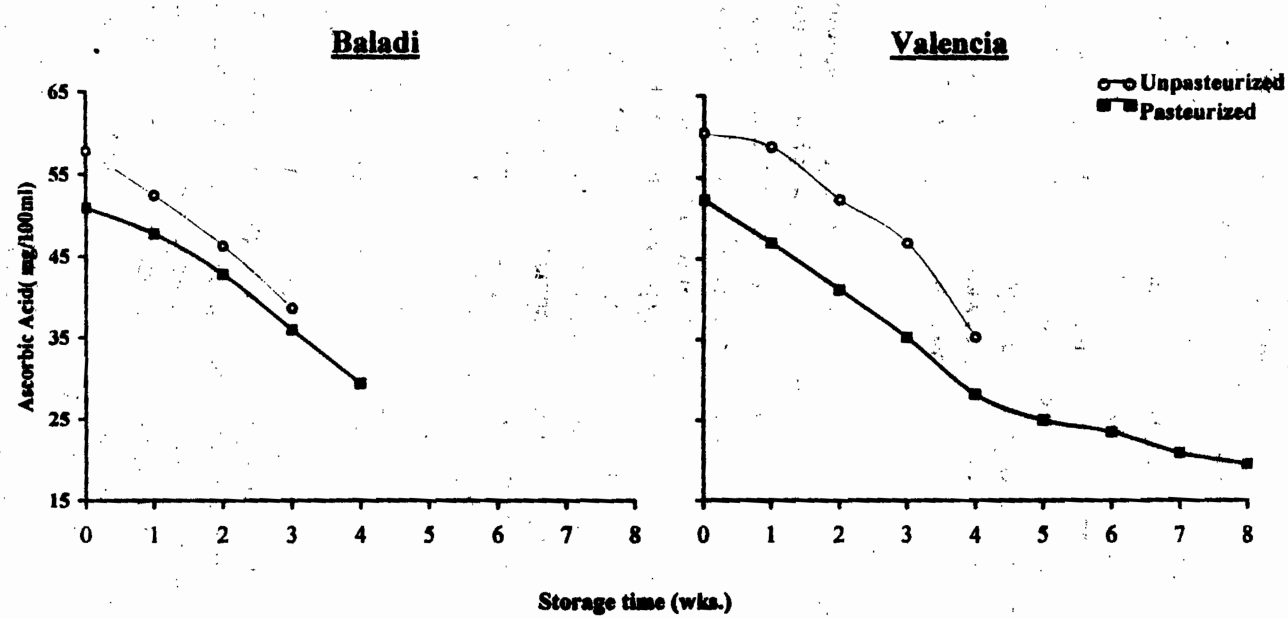

Fig. 6: Effect of pasteurization and cold storage on ascorbic acid of Baladi and Valencia orange juices.

Nagy, 1988; Robertson & Samaniego, 1990 and Kennedy et al., 1992).

In unpasteurized juice, it is most probable that, both ways of destruction take place. Since pasteurization was not employed, the possibility of the native enzymes involvement in vitamin C destruction can not ruled out. Moreover, the presence of oxygen in the juice may lead to aerobic destruction of vitamin C.

The concentration of vitamin C was dramatically reduced at the end of storage period. Pasteurized Baladi orange juice had vitamin C concentration of 17.84 mg/100 ml juice, indicating that 65.50% of vitamin C were lost during storage for 5 weeks. On the other hand, the pasteurized Valencia orange juice had almost the same concentration 18 mg/100 ml juice showing a total loss of 65.57% vitamin C over storage period.

There are many factors that affect the loss of vitamin C during storage such as length of storage, temperature of storage, nature of storage container (Nagy, 1980; Kanner et al., 1982; Marcy et al., 1984; Lee & Coates ,1999 and Farnworth, 2001).

5. Free amino nitrogen:

Free amino nitrogen in orange juices is determined using formol or formaldehyde test which measures the level of primary amino acids. Fig.7 shows that fresh squeezed Baladi and Valencia orange juices contained the same level of free amino nitrogen, being 8.4 mg/100 ml juice. Pasteurization resulted in reduction in free amino nitrogen content in Baladi orange juice, while it increased in Valencia orange juice.

During cold storage, the level of free amino acids found in both unpasteurized and pasteurized juice showed gradual reduction. This can be explained by the sugar-amine condensation through Millard reaction.

6. Browning index:

Browning index is a measure for the browning reactions occurring in orange juice as a result of heat treatment and storage. Fig. 8 shows that browning index was slightly higher in unpasteurized Valencia orange juice when compared to unpasteurized Baladi orange juice . Pasteurization affected the color of Valencia orange juice, while in case of Baladi orange juice there was not marked effect. Storage of unpasteurized orange juices resulted in the increase in browning index. Browning reactions in orange juice can be ascribed to Millard reaction as oxidation of ascorbic acid.

7. Carotenoids:

Concern to carotenoids concentration Fig. 9 unpasteurized

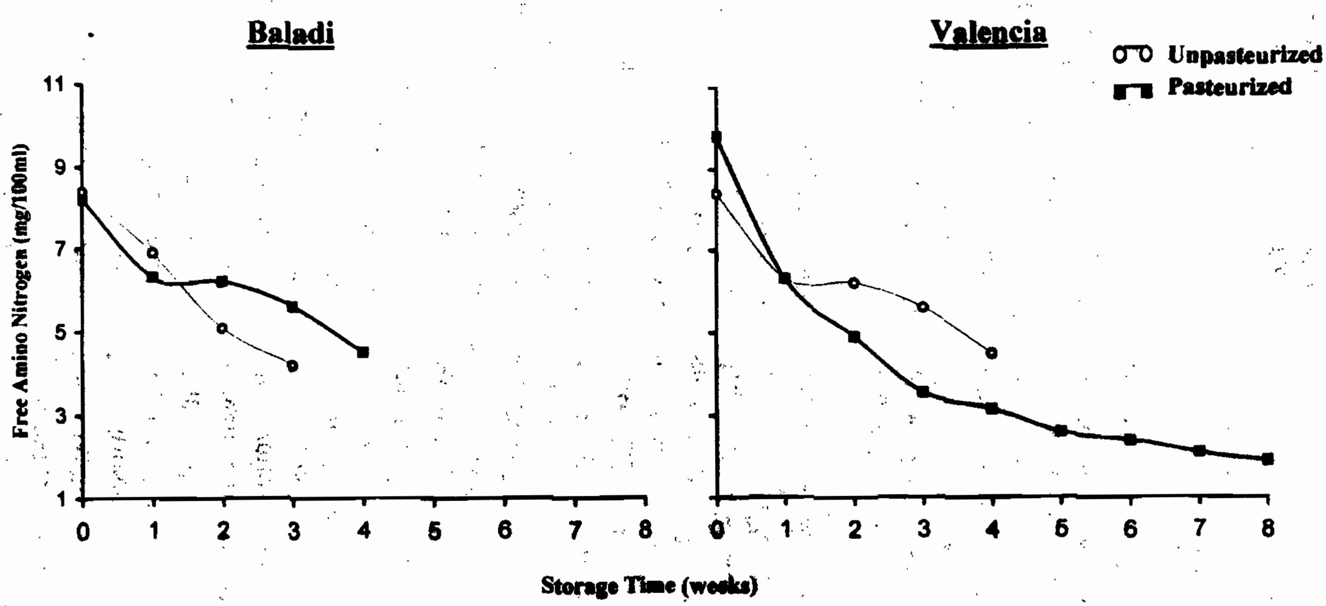

Fig. 7: Effect of pasteurization and cold storage on free amino nitrogen of Baladi and Valencia orange juices.

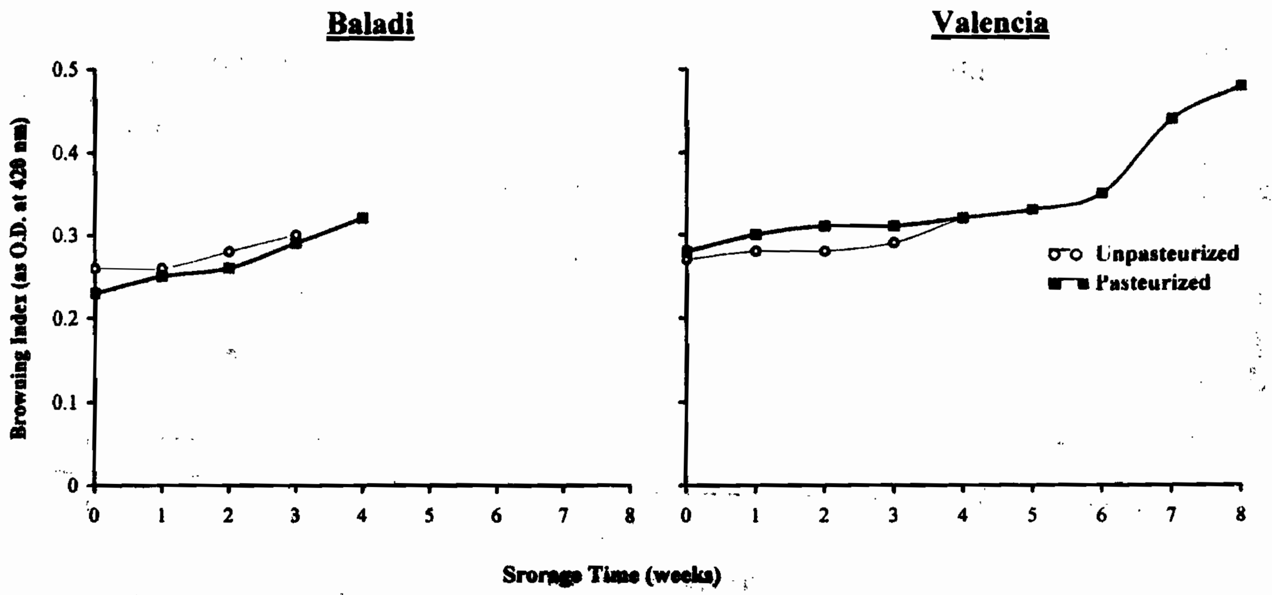

Fig. 8: Effect of pasteurization and cold storage on browning index of Baladi and Valencia orange juices.

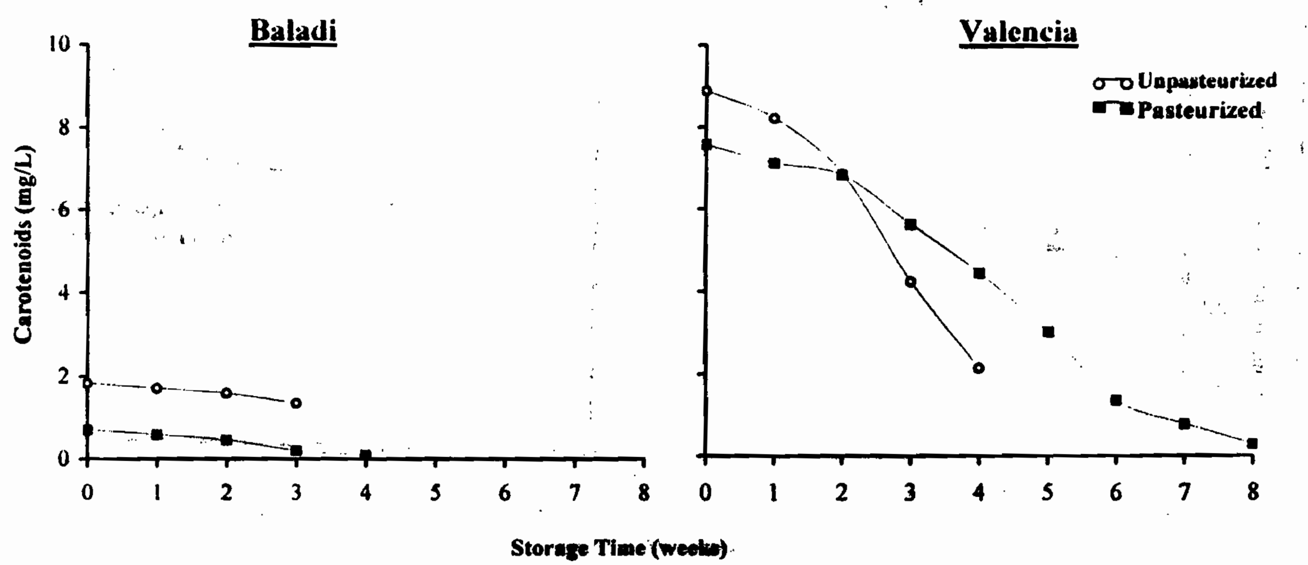

Fig. 9 : Effect of pasteurization and cold storage on carotenoids of Baladi and Valencia orange juice.

Baladi orange juice had considerably lower carotenoids content (1.84 mg/L) than that found in unpasteurized Valencia orange juice (8.90 mg/L). This *indicates that unless blended* Baladi orange juice with other carotene-rich juices will have poor color, while that of Valencia orange pure juice will be accepted. Mouly et al., (2000) found that pure Valencia juices from oranges grown in Mediterranean regions (Israel and Spain) had higher carotenoids concentration, expressed in β-carotene (5-18 and 14-35 mg/L, respectively), compared to those grown in tropical and subtropical regions (Cuba, Belize and Florida; 4-10, 2-8, 5-10 mg/L, respectively).

Pasteurization lowered the content of total carotenoids in Baladi orange juice by 60.87%; while that in Valencia orange juice was lowered by 14.83%. Fig. 9 also shows that, carotenoids content was subjected to gradual decrease during storage of unpasteurized as well as pasteurized orange juices. Destruction of carotenoids in processed and stored foods can follow a variety of pathways, *depending on reaction conditions* (Tannenbaum et al.,1985).

It can be concluded that thermal pasteurization as well as storage at at 8°C resulted in marked changes in chemical constituents of freshly-squeezed orange juice.

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التغيرات الكيماوية في عصير البرتقال البلدي والفالنشيا غير المبستر والمبستر أثناء التخزين بالتبريد

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تصمم المعاملة الحرارية المستخدمة في تصنيع عصير البرتقال لتثبيط الميكروبات الملوثة وإنزيم البكتين استيريز والإنزيمات الأخرى غير المرغوبة، ولكنها قد تغير من خواص العصير الكيماوية والطبيعية. ويهدف هذا البحث إلى دراسة التغيرات التي تحدث في المركبات الكيماوية بعصير البرتقال البلدي والفالنشيا نتيجة للبسترة والتخزين على ٨°م. ووجد أن عصير البرتقال البلدي الطازج غير المبستر يحتوي على ١١,٥° بركس مواد صلبة ذائبة، ١,٢٨% حموضة، ٥,٢٢% سكريات مختزلة، ٣,٨٦% سكريات غير مختزلة، ٥٧,٨ ملليجرام/١٠٠ ملليلتر فيتامين ج، ٨,٤ ملليجرام/١٠٠ ملليلتر نيتروجين أميني حر، ١,٨ ملليجرام كاروتين/ لتر والقيم المقابلة لهذه القيم الموجودة في عصير البرتقال الفالنشيا كانت ١١,٣، ٠,٩٣، ٣,٩٦، ٤,٥٢، ٦٠,٤، ٨,٤ و٨,٩٠ . أدت عملية البسترة إلى انخفاض محتويات كل من فيتامين ج والكاروتينيدات في حين أن ارتفعت محتويات المواد الصلبة الذائبة والحموضة. لم يتغير تركيز السكريات المختزلة وغير المختزلة. كما لوحظ زيادة واضحة في مؤشر التلون البني في العصير. أظهر التخزين على ٨°م بوضوح انخفاض المواد الصلبة الذائبة، فيتامين ج ، النتروجين الأميني الحر والكاروتينيدات بينما ارتفعت الحموضة.

ويمكن الاستنتاج بأن البسترة الحرارية تغير من الصفات الكيماوية لعصير البرتقال ويجب استخدام بسترة باردة بديلة مثل استخدام الضغط العالي وذلك للمحافظة على الخواص التغذوية والجودة لعصير البرتقال الطازج غير المبستر .