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INFLUENCE OF STORAGE ATMOSPHERE ON SHELF STABILITY OF DHAKKI DATES

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ABSTRACT

The date palm (*Phoenix dactylifera* L) cultivar Dhakki of Dera Ismail Khan (NWFP) is very popular for its extra large size, small stone, relish taste, and for being economically important cash crop. However, its keeping quality is affected at the prevailing elevated summer temperatures around (40-50 ^oC). Present research work was started to identify the impact of storage atmosphere on the shelf stability of Dhakki dates at such a high temperature of 40°C. The dates equilibrated at 0.52, 0.58 or 0.75 a_w were packed into tin containers with nitrogen or oxygen as a headspace atmosphere. The control was packed under air to compare the effectiveness of the treatments. The packed samples were stored for 4 months in thermostatically controlled oven at 40°C and were analyzed on monthly basis. Browning and titratable acidity increased whereas the pH declined gradually during the storage. The samples which sustained higher increases in the browning had overall greater pH drop and higher acidity index. The rate of quality degradation appeared to be a function of storage atmosphere and water activity. The quality deterioration in samples stored under nitrogen and equilibrated to lowest water activity of 0.52 a_w eventuated as minimum. The averaged rate of quality degradation in terms of darkening, pH and titratable acidity was found respectively about 2.2, 2.8 and 2.7 times rapid under oxygen compared to under nitrogen, whereas control/air stored samples were approximated in-between nitrogen and oxygen. Nitrogen as headspiece atmosphere together with reduced water activity level extended storage stability bette than oxygen and control for Dhaki dates.

Key words: *Phoenix dactylifera,* inert atmosphere, water activity, quality changes, darkening, pH, titratable acidity.

INTRODUCTION

The date palm (*Phoenix dactylifera* L.) imparts close and everlasting association with mankind, and is legend for the Arabic world. In the Holy Quran, the date is referred at 20 places. Prophet Muhammad (PBUH) enjoyed his followers to honor it as a blessed tree, and since then the date palm became a symbol of Muslim culture. During 'Ramadan', which is annual fasting month for Muslims, the daily fast is broken at sunset with a few dates before taking sips of water. Date palm nourishes millions all over the world and contributes significantly towards their development and prosperity particularly to those living in Arabian world. Since the dates are excellent source of energy and nutrition with high carbohydrates, fiber and potassium but low in fat and almost free from cholesterol and sodium, so these are taken as a staple diet for health conscious persons in particular. Date constitute about 11% of the world total fruit production (Anonymous, 2002), and Pakistan is the 4^{th} largest producer (Anonymous, 2003). It is an important cash crop of Pakistan and a good source for foreign exchange earnings.

Dhakki is the most promising cultivar among the local varieties. Its fruit is popular for its large size (4-5 cm long and 2-3 cm thick) and weight (16-20 gm/ fruit) with fine texture and relish taste, and hence fetches a high price in the market (Baloch, 1999). However, date crop suffers heavy damages by rain and storm due to concurrence of monsoon season with date ripening period. The losses are even greater in case of Dhakki date, which is late variety, and very susceptible at mature/ ripened stage to hot humid climate. Moreover, date production is at a peak during this period and a large quantity of the fresh fruit exceeding need of local consumption is left over, and hence the local market becomes glutted. Due to lack of appropriate processing and storage facilities the surplus produce is wasted.

Moreover, a rapid darkening has been noted in the dates on storage at the prevalent summer temperature of 40–50°C, which causes great concern and calls for attention. Vandercook et al. (1979) reported that browning produced by oxidation of phenolic compounds and from sugar involvement are the main factors responsible for the darkening at elevated temperatures. Rygg (1977) suggested inert atmosphere or vacuum packing for storage of high moisture dates. It was indicated that storage stability depended upon water activity of Dhakki dates and found most stable at about 0.6 a_w (Saleem et al., 1997). The information regarding the effect of storage atmosphere at elevated temperature on stability of dates in general and the Dhakki dates in particular is lacking. The objective of the present study is to explore the potential of inert atmosphere for extending shelf stability of Dhakki dates at a normally prevailing summer temperature of 40°C.

MATERIAL AND METHODS

Sample Preparation

Dhakki date at Khalaal stage with 200–250 mm $Hg.cm^{-2}$ hardness index was purchased from the local market. Well-developed fruits having good appearance were taken, and mixed thoroughly to have a uniform sample. The fruits taken in a wire-mesh basket were treated with sulfite by dipping in 0.5% potassium metabisulfite solution (1kg/L) at 70°C for one minute. The treatment applied so as to retain normal color and flavor of the dates during subsequent process of curing/ drying. The treated sample was allowed to drain, and then taken on to stainless steel trays with single layer loading of 6 kg/m^2. The samples were kept in a Pak-made thermostatically controlled cabinet dehydrator equipped with hot air overflow system at 40°C for 10 hours until the samples were cured and dried to about 24 % moisture contents.

Storage Studies

The dates were thoroughly mixed to ensure sample uniformity, and then divided into three sets of 250 g each for water activity adjustment to 0.52, 0.58 or 0.75 a_w. The samples were equilibrated separately to a specific water activity by keeping samples inside desiccators containing saturated salt solution of a specific water activity for 5 days (Saleem et al., 1997). Each set of equilibrated samples was further divided into three lots for keeping the samples under controlled atmosphere of oxygen, air (control) or nitrogen. Samples (50g) each was taken separately into 250-

size tin-plated canes having two nozzles (valve-built-in) on cross sides for gas flushing. The lid of the cans was sealed hermetically using double seamier. For keeping the samples under a desired controlled atmosphere with specific water activity each can was evacuated (125mm Hg) for one minute and the vacuum released with oxygen–free nitrogen or oxygen. Passing the gases through the desiccators having saturated salt solution of the required water activity performed the gas flushing. To ensure complete change over of the headspace atmosphere the process repeated four times before soldering the nozzle outlets. The samples were also packed under air in order to compare the effectiveness of the headspace atmosphere. The sealed samples were then incubated in an oven for 4 months at 40°C (a temperature that normally prevails during the date harvesting season).

The samples for a selected headspace and water activity were taken out from the storage for periodic analysis after every month. Pits were removed from the dates, cut into small pieces and then ground to a uniform paste. A 2% (w/v) extract was employed for browning, pH and titratable acidity determinations. The browning was determined on the clarified extract by taking absorbance at 420 nm using spectronic-20 spectrophotometer, Busch and Lamb, USA, and a sample showing 0.1 units absorbence was considered brown and shelf life exhausted (Baloch *et al.*, 1997). The pH was measured potentiometrically using digital pH-meter (Model 3010, Jenway England) equipped with temperature control probe. Total acidity expressed as percent citric acid (mg/g) was assessed by titration with 0.1N sodium hydroxide solution using pH-meter. The experiment was conducted simultaneously, and the data analyzed statistically using MSTAT-C (1987) version 2.10 software package applying completely randomized design, and LSD determined after ANOVA for highly significant results. Slope of the plots for measured parameters versus storage period was taken as a rate of quality change, and the effectiveness of a treatment evaluated.

RESULTS AND DISCUSSION

1. Browning

The browning of all the samples remained on the increase during storage at 40°C, however the rate of increase was influenced substantially by the headspace atmosphere and the water activity of the samples (Fig. 1). The samples showed maximum darkening (0.089) after being stored under oxygen, whereas a minimum amount (0.059) is displayed under the nitrogen at the same water activity. The mean values as regard to atmosphere are statistically significant ($P < 0.05$) (Table 1). The rate of the darkening for a sample at 0.75 a_w stored under the oxygen headspace was 12.1 $x10^{-3}$ /month as compared to 8.6 $x10^{-3}$ /month under air, and 5.2 $x10^{-3}$ /month under the nitrogen (Fig. 2). The samples appeared more than twice stable under the nitrogen as under the oxygen, and looked normal in color and flavor at end of the storage, whereas those under the oxygen appeared dark brown with a smell of burnt sugar. A continuous increase in darkening of samples under air, oxygen or nitrogen headspace indicates the involvement of oxidative as well as non-oxidative deterioration during the storage (Vendercook et al., 1979). This might be due to fact that the cured dates at tamar stage possess carbohydrates (sugar), amino acids and tannin polyphenolic compounds (Sawaya et al., 1982), which are likely to induce darkening under both aerobic and anaerobic conditions (Maier and Metzler, 1965). However, the oxidative deterioration appeared to be more than twice as fast as the non-oxidative. Maier and Schiller (1960) reported that browning caused by sugars predominates at temperature above 38°C, and the darkening at 49°C followed primarily by non-oxidative and non-enzymatic routes. However, Maier and Schiller in (1961 a and b) made both oxidative and non-oxidative deteriorative reactions responsible for the darkening in Deglet Noor at 38°C. They further reported that the former caused 20% greater darkening, which was inhibited by storage under inert gas. In case of Dhakki dates however, the darkening was reduced by more than 30% on storing the samples under the nitrogen environment. Mohsen et al. (2003) noted vacuum packaging a useful technique for reducing darkening of the dates for long term storage.

Mechanism for the browning in model systems (Hodge, 1953), as well as in fruits and vegetables along with its control by sulphite had been reviewed thoroughly (McWeeny et al., 1974: Wedzicha, 1987). In the present study the Dhakki dates were given a mild treatment with sulphite in order to avoid changes during the process of curing and drying.

The water activity of the samples also played important role in controlling the darkening. Adjusting the samples at a reduced water activity of 0.52 a_w the stability of the date samples was increased under any headspace (Fig. 1, Table 1), and the rate became 1.21 to 1.30 times slower on reducing water activity of samples from 0.75 to 052 a_w. The highest stability was with the sample having lowest water activity and stored under nitrogen, and the findings are consistent with those reported by Mutlak and Mann (1984) and Saleem et al. (1997). The mean values of samples as regards to water activity are statistically significant ($P < 0.05$), however, no significant difference was seen between the samples with 0.52 and 0.58 a_w (Table 1).

2. pH Changes

Irrespective of the environment under which the samples were stored the pH showed a gradual decline from pH 6.3 to 3.58 during the storage (Fig. 3). Maximum pH drop of 2.72 units was observed in case of the samples enclosed under the oxygen with 0.75 a_w (equivalent to $6.75x10^{-1}\Delta pH/mo$, Δ stands for change). Whereas the corresponding reduction of 1.6 and 0.92 pH units was noted for air and nitrogen (Fig. 3, Table 1) and hence reducing the rates by 1.74 and 3.11 times respectively (Fig.4). Similar observations are reported by Maier and Schiller (1961a) in case of Deglet Noor variety. The effect of the atmosphere was statistically significant ($P < 0.05$, Table 1). A continuous decline in pH for all samples under any storage atmosphere advocates the involvement of both oxidative and non-oxidative mechanism as noted earlier in case of the darkening. It is once again indicated that the storage under inert atmosphere along with the lowest selected water activity was the most effective measure for controlling the deteriorative changes.

Water activity of the samples also played a vital role in governing pH changes, and samples with reduced water activity displayed resistance against the deterioration. The effectiveness of lowering water activity became more prominent on exposing samples to oxidative environments. About 29 % reduction in the rate of pH change occurred for samples under the nitrogen on reducing water activities from 0.75 to 0.52 $a_{w,}$ whereas the corresponding reduction for air and oxygen were from 37 to 38 %. The rate however, slowed down overall by 77 % on changing water activity from 0.75 to 0.52 a_w and atmosphere from oxygen to nitrogen. The process causing pH change follows mainly an oxidative pathway similar to that speculated for the darkening process. The study reveals that storing of samples at inert environment (nitrogen) along with lower water activity of 0.52 a_w had positive impact for maintaining pH. The mean values for pH regarding the effect of water activity were found statistically significant ($P<0.05$, Table 1). The manifestation that the samples which showed increased rate of darkening corresponded to increased rate of pH drop on subjecting to same environmental stresses, demonstrating that there is a common reaction sequence which leads to the formation of brown color as well as brings changes in pH.

3. Titratable Acidity

A consistent rise in titratable acidity was observed for all the samples during the storage (Fig. 5). However, the rates were greatly influenced by making changes in the storage atmosphere and water activity. Acidity prior to storage ranging from 22.15×10^{-2} to 22.37×10^{-2} (mg/g) increased to 43.57×10^{-2} to 100.95×10^{-2} (mg/g) by keeping the equilibrated samples within 0.52 a_w to 0.75 a_w for 4 month at 40 °C under oxygen, nitrogen or air atmosphere, respectively. The rate of acid formation of 19.14 /month was highest in samples equilibrated with 0.75 a_w and stored under oxygen, but it appeared as a minimum of 5.43 /month in the samples with 0.52 a_w and stored under the nitrogen atmosphere. The rate of acid formation in the samples with 0.75 a_w was about 1.76 and 2.86 times higher under oxygen than for those under air or the nitrogen respectively (Fig. 6), and the mean values for titratable acidity regarding atmosphere and water activity are statistically significant ($P < 0.05$, Table 1). It is further noted that the samples which yielded higher amount of darkening had produced relatively greater amount of increase in the titratable acidity with simultaneous decrease in pH. Since there is a great concordance amongst the deteriorative reactions leading to darkening, acid formation and pH changes it is apprehended that all such reactions had a common pool from where these are emerging out. Present findings are in line with those reported by Saleem et al. (1997) and Saddozai et al. (1998) who had also shown similar increase in acidity with coexisting decrease in pH during storage of Dhakki dates and milk concentrate 'Khoa' respectively.

CONCLUSION

The browning, acid formation, pH changes and other associated deteriorative reactions are the function of storage atmosphere and water activity of Dhakki dates. Since the samples were stored at elevated temperature of 40°C and at water activity within the range of intermediate moisture limits, the degradative reactions possibly interacting with each other, eventuated at very rapid rate. Packaging the samples under nitrogen environment and at lower water activity level proved to be useful measures for controlling deteriorative changes. The study suggests that Dhakki date preferably be stored under atmosphere free from oxygen and at water activity close to 0.6 a_w so that the product maintains high quality and sufficient stability with extended shelf life.

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TABLES

Table 1: Mean values for darkening, pH and titratable acidity as affected by storage atmosphere and water activity of Dhakki dates at 40°C for 4-months

Factors → ↓		**Darkening**	**pH**	**Titratable acidity**
Headspace atmosphere	Oxygen	0.060 A	5.12 C	52.67 A
	Nitrogen	0.049 C	5.79 A	32.02 C
	Air	0.055 B	5.53 B	39.80 B
Water activity (a_w)	0.52	0.053 Y	5.58 X	38.28 Z
	0.58	0.054 Y	5.52 Y	40.36 Y
	0.75	0.065 X	5.34 Z	45.85 X

Mean values bearing different letter (A–C), (X–Z) in each column for every factor differ significantly (LSD, P ≤ 0.05).