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Pre-treatments of Tas-A-Ganesh grape bunches and subsequent effect on their drying

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ABSTRACT

The pre-treatment of Tas-A-Ganesh bunches affected the quality parameters of raisins when bunches were dried under raisin sheds. Various combinations of ethyl oleate and potassium carbonate affected the moisture content and other quality parameters of raisins. The dynamics of changes in content of moisture and colour intensity was also affected by pre-treatments. The contents of phenols, flavonols, flavonoids and flava-3-ols in the raisins were also significantly affected by the pretreatments. Application of 15 ml/l ethyl oleate and 25 g/l potassium carbonate for 2, 4 and 6 min. significantly affected the moisture content, colour intensity and content of other colour contributing substances, *viz*., phenols, flavonols, flavonoids and flavan-3-ols of raisins. Increment in pre-treatment duration resulted in early drying and raisins obtained had lower colour intensity. The best quality raisins (15.9%) were observed by pre-treatment of grape bunches with solution of 15 ml ethyl oleate and 30 g/l potassium carbonate.

Key words: Grape, pre-treatments, drying, quality, raisins.

INTRODUCTION

Raisins are one of the most important dried products obtained by drying of grapes. In India, raisin is mostly produced in Sangli and Solapur districts of Maharashtra and Bijapur district of Karnataka. The key to the quality of raisins is the drying process and their water content. Generally, three drying methods are employed to produce raisins; sun drying, shade drying and mechanical drying. Drying practices vary with geographical locality and with the variety of grapes (Pangavhane and Sawhney, 10). The quality of the dried products implies that several desirable changes (physical, chemical, and biochemical) must occur during the drying process. Pre-treatment of bunches in oil emulsion is common practice followed in India for making good quality raisins. It is observed that grape samples which were pre-treated with oleic acid and potassium carbonate solutions, dried faster than the untreated samples. The oleic acid dipping has increased the drying rates according to the potassium carbonate pretreatment and appearance of the dried grapes. Oleic acid has destroyed the resistance of waxy layer which prevents moisture transfer and increased the drying rate (Ismail *et al.*, 8). Different alkaline solutions such as simple soda solution, potassium carbonate with olive oil, carbonate with olive oil as well as "alkaline rock" are used (Salunkhe and Desai, 15). "Alkaline rock" is extracted from *Salsola soda* (a plant species locally called '*Shoran*' or '*Eshnabian*') which has been historically used for raisin production in some regions in Iran (Arzani *et al*., 2). Apart from chemical components (either “alkaline solutions with or without dipping oils” or “compounds such as ethyl oleate with or without alkaline solutions”), the pre-treatments will cause an increase in the drying rate particularly at the early stage of drying process. The composition, concentration, pH and temperature of the chemicals and the pre-treating time are effective factors in microstructural changes of the skin layers (Esmaiili *et al.*, 6). Today, most commercial cold dips utilize a combination of potassium carbonate and ethyl esters of fatty acids (commonly referred to as ethyl oleate) as active constituents in unheated water hence the term cold dip. This treatment increases the rate of water loss twofold to three-fold, an important factor in countries where drying conditions are very unpredictable. The type of chemical pretreatment and origin of the product significantly affect the drying behavior of the grapes (Christensen and Peacock, 4). The physical characteristics of raisins from different countries are quite different, while chemical characteristics being fairly consistent. The physical characteristics are probably the result of cultivars, cultural, and processing differences (Bongers *et al*., 3). It has been reported that the aim of using pretreatment solutions is to increase drying rates and to produce raisins of a more desired quality level (Doymaz and Pala, 5). The use of ethyl oleate as pre-treatment solution for the drying of grapes leads to a better colour (L and a = b values). Colour of the treated grapes was lighter than that of the

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untreated grapes. Colour of the final product could be influenced by the state of fresh fruit. Sunlight exposure affects grape composition, especially the phenolic compounds in the skin (Spayd *et al*., 17). Considering the effect of pre-treatments and duration on grape drying and subsequent product, *i.e.*, raisin, this study was conducted with aim to standardize the combination of ethyl oleate and potassium carbonate and dipping duration in relation to lower colour intensity and other colour contributing parameters in raisins.

MATERIALS AND METHODS

This study was carried out at National Research Centre for Grapes, Pune (India) during 2010. Bunches of Tas-A-Ganesh a mutant of Thompson Seedless (TSS value of about 23°Brix, pH 3.73 and TTA 4.7g/l) were used for raisin preparation. The following combinations of ethyl oleate and potassium carbonate were applied; A_1 = 10 ml ethyl oleate + 20 g potassium carbonate, A_2 = 10 ml ethyl oleate + 25 g potassium carbonate, A_3 = 10 ml ethyl oleate + 30 g potassium carbonate, A_4 = 12.5 ml ethyl oleate + 20 g potassium carbonate, A_5 = 12.5 ml ethyl oleate + 25 g potassium carbonate, A_6 = 12.5 ml ethyl oleate + 30 g potassium carbonate, A_7 = 15 ml ethyl oleate + 20 g potassium carbonate, A_8 = 15 ml ethyl oleate + 25 g potassium carbonate, A_9 = 15 ml ethyl oleate + 30 g potassium carbonate. The pH values of these combinations varied 10-11. Ten kg grape bunches were dipped in 5 l solution in each treatment. Bunches of uniform size were dipped in above (A_1 to A_9) combinations for 2 min. These pre-treated bunches were spread on racks inside a raisin shed. In another experiment, the bunches were dipped in a combination of 15 ml ethyl oleate + 25 g/l potassium carbonate for 2, 4 and 6 min. To avoid exposure of bunches from direct sunlight, eastern, southern and western sides were covered by curtain whenever required. The raisin had racks with nylon mesh to provide proper ventilation and light to berries from lower side. The treated bunches were spread on racks (5 to 6 kg grape bunches/ sq. m) for drying with regular turning up everyday to provide even temperature, wind velocity and light intensity to every part of the bunch during drying process. The mean temperature during drying process was varied between 28-32°C. The samples were collected as per plan to study changes in dynamics of moisture loss and colour intensity as influenced by pre-treatments. After a drying duration of 10 days, the samples of raisins were collected for analysis.

Standard procedures were followed for analysis of quality parameters, like moisture content (Anon, 1). For estimation of total phenols, flavonols, flavan-3-ols, flavonoids, and colour intensity, 10 g of sample was crushed making paste with 15 ml of 80% methanol with mortar and pestle and collect in centrifuge tubes (30 ml). Centrifuge tubes were kept overnight with shaking (Scigenics-Orbitek, RPM 250, temperature: ambient temperature) for proper mixing. Then it was kept for centrifugation (Kubota- High Speed centrifuge 6500) at 5,000 rpm for 5 min. and supernatant of first extract was collected in a sampling box. Again it is kept for overnight shaking after addition of 10 ml methanol (80% v/v). Next day it was centrifuged again at 5,000 rpm for 5 min. and supernatant of second extract of same sample was collected. Both the collected extracts were filtered through 0.45 μ filter paper (Whatman No.1) and pure extract was collected in a new sampling box and kept at 0°C till analysis. Total phenolic content in the samples were determined with Follin-Ciocalteu reagent (Slinkard and Singleton, 15) by using gallic acid as standard phenolic compound. The content of flavan-3-ols was estimated by method of dimethylaminocinnamaldehyde (DMACA) and to quantify concentration of total flavonoids (Zhishen and Jianmize, 18). Colour intensity was determined by taking observance on 420, 520 and 620 nm by using UV-VIS spectrophotometer (UV-Pharmaspec v1700, Shimadzu) as per method suggested by Somers and Evans (16). Three replicates were taken for each samples per treatment. The generated data were statistically analyzed as suggested by Panse and Sukhatme (11).

RESULTS AND DISCUSSION

The combinations of ethyl oleate and potassium carbonate significantly affected various quality parameters of raisins. The moisture content ranged from 15.9 to 20.6 per cent in A9 and A4, respectively. At early stage of drying, faster drying was observed in A4 (Fig. 1) but combination of 15 ml ethyl oleate and 30 g potassium carbonate/l showed superiority over other combinations (Table 1). The dynamics of colour intensity was also affected by pretreatment of bunches with various combinations of ethyl oleate and potassium carbonate (Fig. 2). In early days of drying process, colour intensity was lower in A2 but after 8th day, minimum colour intensity was observed in A9. Maximum colour intensity (22.6) was observed in A1 after 3rd day of drying. The differences in the colour intensity from treatment, *viz*., A7, A4, A3 and A2 were non-significant. Minimum colour intensity (15.0) was recorded in treatment of bunches with solution of 15 ml ethyl oleate + 30 g potassium carbonate, which closely followed by treatment with 15 ml ethyl oleate + 25 g potassium carbonate with the value of 15.6 (Table 1). The contents of phenols, flavonols, flavonoids and flavon-3-ols in the raisins were also significantly affected by the pre-treatments. The concentration of phenols in raisins increased with increment in concentrations of ethyl oleate and potassium carbonate. Minimum

Table 1. Physico-chemical parameters of raisins as affected by pre-treatments of bunch with various combinations of ethyl oleate and potassium carbonate.

Pre-treatment	Moisture (%)	Colour intensity	Phenols (mg/g)	Total flavanols (mg/g)	Total flavanoids (mg/g)	Total flavan-3-ols (mg/g)
A_1	18.6	22.6	14.62	4.08	11.1	0.24
A_2	20.4	17.7	16.10	4.01	9.3	0.15
A_3	17.9	17.4	17.04	2.76	9.0	0.14
A_4	20.6	17.1	14.72	3.00	9.0	0.35
A_5	17.8	16.4	15.19	2.65	9.3	0.19
A_6	17.5	16.0	17.28	2.64	10.8	0.21
A_7	17.0	17.0	16.22	3.93	9.7	0.23
A_8	16.9	15.6	19.31	3.32	8.4	0.21
A_9	15.9	15.0	20.45	3.17	8.7	0.18
CD at 5%	0.13	0.769	2.399	0.126	0.381	0.083

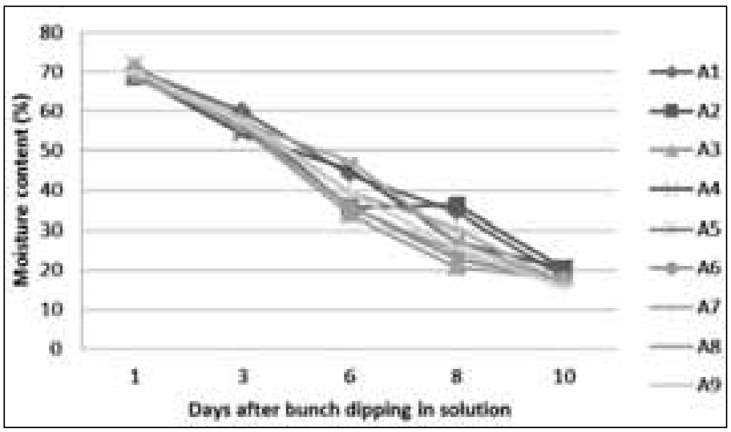

Fig. 1. Moisture content (%) during grape drying as affected by various combinations of ethyl oleate and potassium carbonate.

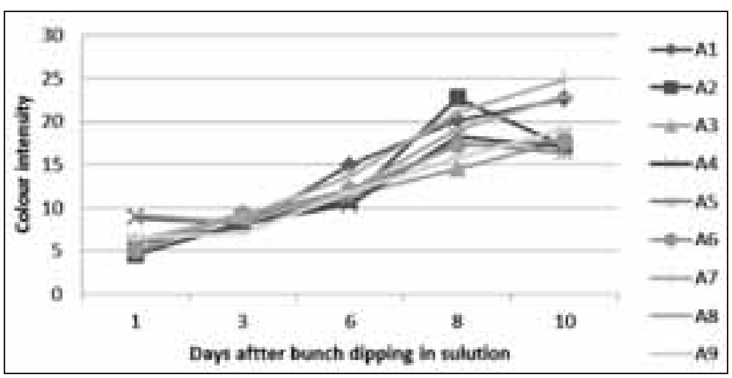

Fig. 2. Colour intensity during drying process of Tas-a-Ganesh grapes as affected by pre-treatments of bunches.

phenols (14.62 mg/g) were recorded in treatment of bunches with the solution of 10 ml ethyl oleate + 20 g potassium carbonate and the highest value of phenols, *i.e.*, 20.49 mg/g was noted in treatment of bunches with the solution of 15 ml ethyl oleate + 30 g potassium carbonate. The combination of ethyl oleate and potassium carbonate significantly affected the content of total flavonols, flavonoids and flavon-3-ols. The content of flavonols and flavonoids in raisins showed a declining trend from 4.08 to 2.64 and 11.1 to 8.4 mg/g, respectively with increase in strength of ethyl oleate and potassium carbonate, *i.e.* from 10 to 20 ml ethyl oleate and 20 g potassium carbonate to 15 ml ethyl oleate and 30 g potassium carbonate in the solutions used for pre-treatment.

The impact of dipping treatments was also observed in various quality parameters. The colour intensity and colour contributing substances were significantly affected by duration of bunch dipping from 2 to 6 min. in the solution of 15 ml ethyl oleate + 25 g/l potassium carbonate. The moisture content of raisins was significantly affected by dipping durations. Rise in dipping duration resulted in lower moisture content, which indicated faster drying of grapes. Dipping duration of 6 min. was recorded with only 14.94 per cent moisture while in case of 2 min. dipping duration, it was 16.65 per cent after 10 days of pre-treatment (Table 2). Reduction in colour intensity of raisins was recorded with increasing dipping duration of bunches in solution. The colour intensity of raisins obtained from treatment of 2 min. was 18.50, which declined up to 12.56 in the treatment of bunches for 6 min. The content of colour contributing substances, *viz*., flavonoids and flavon-3-ols decreased in the raisins with increase in duration of bunch dipping in solution, while contents of phenolics and flavonols were increased by 89.3 and 15.1 per cent, respectively. The phenolics increased from 12.34 to 23.36 mg/g.

The moisture loss during drying of grapes is affected by pre-treatments of grape bunches. Various combinations of ethyl oleate and potassium carbonate fastened the moisture loss from the berries. Due to application of various combinations of ethyl oleate and potassium carbonate, different moisture contents were recorded in the raisins at the same drying time. Earlier, Nicoletti Telis *et al*. (9) found that the pre-treatments were effective in accelerating the drying process, with lower moisture contents in grapes treated with an emulsion of 2.5% olive oil and 6% potassium carbonate. The ethyl oleate changes the primary structure of the waxy platelets pushing them apart and helping to establish a water conductivity link. The potassium carbonate neutralized acids and is a necessary component of the drying aid. It was recorded by Gabas *et al*. (7) that the increasing in concentration of ethyl oleate between 0 and 3% in a solution of 2% $CaCO_3$ increased considerably the drying rates, as well as resulted in a less collapsed structure of raisins. Dipping duration also affect the rate of moisture loss. The increment in dipping duration accelerates the moisture loss, which results in faster drying. The effect of alkaline emulsion of ethyl oleate (AEEO) and potassium carbonate (POTAS) solutions on hot air drying of grapes was studied by Doymaz and Pala (5). It was concluded that the grapes dipped in AEEO or POTAS solution were found to have shorter drying times compared with untreated grapes. The AEEO dipping increased the drying rates more than the potassium carbonate pretreatment and improved the quality and appearance of the dried grapes. Pre-treatment with the AEEO solution is effective in increasing the drying rate during the early period of raisin preparation. The combinations of ethyl oleate and potassium carbonate improved the overall acceptability of raisins by improving colour of the produce. Dynamics of colour intensity during grape drying was influenced by pre-treatments of grape bunches. The browning of untreated grapes during drying is mainly caused by PPO (polyphenol oxidase). The dipping process, used to increase the drying rate, prevents browning, but it does not affect the enzyme or its activity directly. The drying rate is increased without a corresponding increase in oxygen uptake of the fruit, so it is concluded that the enzyme is inhibited by rising sugar concentrations, and not by components of the dipping solution (Radler, 12). However, Doymaz and Pala (5) reported that the pre-treatments also have an important effect on the colour parameters of the final dried products. In terms of desired colour properties, higher L and lower a=b ratio are preferred. Hunter L (lightness) values of grapes dipped in AEEO (dissolving 0:5 kg potassium carbonate in 10 l water and adding 0.2 kg ethyl oleate) solution were in most cases higher than those for grapes dipped in POTAS (solution is prepared by dissolving 0:5 kg K_2CO_3 in 10 l water and adding 0.05 kg olive oil) and naturally dried

Table 2. Effect of duration of dipping on colour intensity and colour contributing substances of raisins.

Bunch dip duration (min.)	Moisture (%)	Colour intensity	Phenolics (mg/g)	Total flavanols (mg/g)	Total flavonoids (mg/g)	Total flavan-3-ols (mg/g)
2	16.65	18.50	12.34	2.82	11.18	0.26
4	16.15	13.39	15.33	3.12	10.23	0.21
6	14.94	12.56	23.36	3.25	9.75	0.20
CD at 5%	0.41	0.41	4.40	0.21	0.36	0.01

grapes. The pre-treatments also affected the content of phenolic compound in the raisins.

The results of present study showed that content of total phenols and other phenolic compounds (flavonoids, flavonols and flavon-3-ols) influenced by pre-treatment of bunches with various combinations of ethyl oleate and potassium carbonate and duration of dipping. In general, except for the phenolic compounds corresponding to the drying with ethyl oleate pretreatment, most of these compounds increased to a lesser extent than expected because of water losses of the grapes during drying, revealing degradation reactions (Serratosa *et al.*, 14). The results of present study indicated that combinations of ethyl oleate and potassium carbonate as well as dipping duration of bunch affected various quality parameters of raisins and improvement in colour of raisins was found with longer dipping duration for 6 min.

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