

Original Research Article

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Studies on Various Concentrations of Antioxidants with Alkaline Emulsion of Ethyl Oleate as Pre-Treatment on Rate of Drying, Yield and Colour of Raisins Prepared from Seedless Grape (*Vitis vinifera* L.)

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ABSTRACT

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The investigation was planned and executed to study the influence of various concentrations of antioxidants (Ascorbic acid, AA 500, 750 and 1000 ppm and Benzyl adenine, BA 50, 100 and 150 ppm) with alkaline emulsion of ethyl oleate (AEEO, 2.4% K₂CO₃ + 1.5% ethyl oleate) as a pre-drying treatment on rate of drying, drying ratio (grape: raisin), yield and colour of raisins prepared from seedless varieties of grapes. The Selected grape bunches of seedless varieties Thompson Seedless (TS), 2A Clone (2AC), Sonaka (SO), Manik Chaman (MC) and Merbein Seedless (MS) were dried in ventilated rooms after pre-drying treatment. Results showed that the raisins prepared by using AEEO with AA 1000 ppm as pre-treatment showed lowest brown and mixed colored raisins, and correspondingly increased percentage of green colored raisins. The berries dried early in variety MS and it takes only 13.64 days followed by 2AC, TS, MC and SO in order. The raisins prepared from variety TS were superior compared to others in terms of drying ratio, raisin yield, raisin waste, average raisin weight. From this finding it can be concluded that the raisins prepared from Thompson Seedless by using alkaline emulsion of ethyl oleate with ascorbic acid 1000 ppm was superior to other varieties.

Introduction

Grape (*Vitis vinifera* L.) is an important commercial fruit crop in India, about 78% of production is used for table purpose; nearly 17 to 20% is dried for raisin production, while 1.5% is used for juice and only 0.5% is used in manufacturing wine. Dried grapes, commonly known as raisins, are of a great economic importance for many countries.

Raisins are a good source of fiber, K, Fe, Ca and vitamin B and are free from fat and cholesterol. They contain only natural sugars as a source of energy. The word 'raisin' originates from the French word 'racemes', which means 'a cluster of grapes or berries'. Historically the production of raisin from grapes by sun-drying can be traced back to

1490 B.C. in Greece (Winkler, 1962). USA, Turkey, China, Iran, Chile, Argentina, Australia and Greece are the main raisins producers in the world (DFTS, 2013). In India, raisins are mainly produced in Sangli, Solapur and Nasik districts of Maharashtra and Bijapur district of Karnataka state from the varieties *viz.*, Thompson Seedless and its clones like Tas-A-Ganesh, Sonaka and Manik Chaman (Adsule *et al.*, 2008). Telangana State falls under semi-arid tropical region wherein the major grape cultivation is confined to Ranga Reddy, Mahabubnagar and parts of Nalgonda district. Since the harvest period (February to May) is during summer with low relative humidity, it is excellent for raisin making. The different varieties of seedless grapes grown here are vigorous and highly productive.

The varied physical characteristics of raisins are probably the result of cultivars, cultural practice followed and processing differences. The technique of raisin production in India is mostly based on the dipping of the grape bunches in emulsion having 2.5% potassium carbonate and 1.5% ethyl oleate for a duration of 2 to 4 minutes, and subsequent shade drying in open tier system (Adsule *et al.*, 2012). The dipping oil treatment alone induced soft texture, but it led to the development of brown rather greenish color. Green coloured raisins are highly valued for their fresh, attractive green color, sweet flavour and sold for two to three times the price of sun-dried raisins.

Antioxidants are the molecules that are capable of preventing the oxidation of other molecules by scavenging reactive oxygen species before they can damage the cells. Application of antioxidants like ascorbic acid and benzyl adenine along with dipping solution *i.e.* alkaline emulsion of ethyl oleate (AEEO, 2.4% K₂CO₃ + 1.5% ethyl oleate) as a pretreatment effectively reduced browning in raisins (Sharma *et al.*, 2012). Green color

retention is one of the major concerns in raisin production; hence, the study was carried out to find the effect of various concentrations of antioxidants on drying, colour and yield of raisins prepared from various seedless varieties of grapes.

Materials and Methods

The experiment was conducted at Grape Research Station, Rajendranagar, Hyderabad in Ranga Reddy district, Dr. Y.S.R. Horticultural University during 2012–14. The Grape Research Station is located at 77°85' East longitude and 18°45' North latitude and at an altitude of 542.6 m above mean sea level. The experimental location falls under semi-arid tropical climatic zone, having annual rainfall of 800 mm.

Selected grape bunches of seedless varieties (V₁) Thompson Seedless (TS), (V₂) 2A Clone (2AC), (V₃) Sonaka (SO), (V₄) Manik Chaman (MC) and (V₅) Merbein Seedless (MS) were manually harvested. The harvested bunches were cleaned, washed in soap water followed by washing in pure water. A solution containing 2.4% potassium carbonate + 1.5% ethyl oleate (*i.e.* alkaline emulsion of ethyl oleate, AEEO) was prepared in a plastic bucket. The pH of the solution was adjusted to 11 while adding potassium carbonate. Dipping solutions of 500 ppm, 750 ppm and 1000 ppm of ascorbic acid (AA) were prepared by dissolving 5 g, 7.5 g and 10 g of AA respectively in 10 litres of AEEO. Similarly 50 ppm, 100 ppm and 150 ppm of benzyl adenine (BA) were prepared by dissolving 0.5 g, 1 g and 1.5 g of BA respectively in 10 litres of AEEO. Then the grape bunches were dipped in the solution prepared for dipping *i.e.* (A₁) AEEO + AA 500 ppm, (A₂) AEEO + AA 750 ppm, (A₃) AEEO + AA 1000 ppm, (A₄) AEEO + BA 50 ppm, (A₅) AEEO + BA 100 ppm, (A₆) AEEO + BA 150 ppm and (A₇) AEEO as a control for 3 minutes, and then kept for shade drying

in trays. Under shade drying, the trays of pre-treated bunches were placed in well ventilated room at ambient condition. Moisture testing of raisins was done frequently for a preserved level (approximately 15% moisture).

After imposition of pre-treatments, the weight of the grapes in each replication was recorded every three days intervals. The rate of drying was obtained by loss of moisture during the drying period (Sharma *et al.*, 2013). The time taken for drying (in days) for pre-treated grapes were calculated when the moisture level in raisins comes to 15 per cent (Parpinello *et al.*, 2012). Drying ratio calculated by the weight of fresh grape to obtained raisins. The weight of 100 raisins of each replication was taken and calculated to obtain average weight of raisins (Adsule *et al.*, 2008). Raisin yield recorded in kilo gram of raisins per vine (Parpinello *et al.*, 2012). The weight of decayed, over shrivelled and damaged raisins was taken and calculated to grams of raisin waste from fresh grapes. The prepared raisins were graded based on color *i.e.* pale green (consider as green in the entire experimentation), brown and mixed (the mixture in which the percentage of dominant color did not exceed 60%). Hundred grams of raisins was weighed and the separation of which was done according to the mentioned color classes (Arzani *et al.*, 2009).

The experimental data were subjected to analysis of variance (ANOVA) using factorial completely randomized design as per the procedure outlined by Panse and Sukhatme (1985). Least significant differences (Fisher's protected LSD) were calculated following significant F-test ($p=0.05$).

Results and Discussion

Rate of drying

The rate of drying was significantly different from the various concentrations of

antioxidants with alkaline emulsion of ethyl oleate (AEEO) during drying period. It was evident from figure 1 that the increased concentrations of antioxidants (*i.e.* Ascorbic acid, AA and Benzyl adenine, BA) with AEEO decreases water loss on 3rd, 6th, 9th, 12th and 15th days after pre-treatment. Various concentrations of antioxidants with AEEO significantly fastened the water loss from the berries on all the days (day 3 to day 15) after pre-drying treatment. Significantly maximum water loss was recorded in AEEO + AA 1000 ppm and minimum in control (*i.e.* AEEO only) during the drying period. The rate of drying was faster in pre-drying treatment A₃ in our study which might be due to the ascorbic acid pre-treatment tends to loosen the water molecules (Abano *et al.*, 2013). Grncarevic (1963) and Bingol *et al.*, (2012) also found that the grapes treated with a cold dip of commercial dipping oil (ethyl oleate + K₂CO₃) enhance the drying rates.

On day 3 and 6, significantly maximum water loss was recorded in Merbein Seedless and minimum in Sonaka (Figure 2). On day 15, it was noted highest in Merbein Seedless and lowest in Sonaka which was comparable with Manik Chaman. In all the days after pre-drying, there wasn't much oscillation between the values of water loss in different varieties of grapes used for raisin making (Figure 2). Comparatively, Merbein Seedless berries were smallest and thin skin which might be the result of early drying compared to other varieties (Chadha and Shikhamany, 1999). The water loss in Sonaka was lower which might be due to more juicer, less pulpy and bigger size berries compared to other varieties. As mentioned earlier, Ramming (2009) and Christensen and Peacock (2000) also observed differences in drying rate between the cultivars and suggested that cultivar differences in berry cuticle and skin influence drying rate. The interaction effect on water loss between various concentrations of antioxidants with AEEO and varieties was

not significant in all the days after pre-drying treatment.

Drying ratio (grape: raisin)

The results related to drying ratio (fresh grapes to obtained raisins) as influenced by various concentrations of antioxidants with AEEO as pre-drying treatment in seedless grape varieties are depicted in table 1. A minimum of 3.99 kg of fresh grapes were required to obtain 1 kg raisins in pre-drying treatment AEEO + AA 1000 ppm (A₃) whereas a maximum of 4.18 kg was required to obtain same amount of raisins in control (A₇). It was recorded to be lowest in (A₃) which may be due to the ascorbic acid play major role in drying (Figure 1) which ultimately leads to lower drying ratio (Farouk, 2011). The drying ratio also significantly influenced by grape varieties used for raisin making. It was significantly lowest in Thompson Seedless (3.87) whereas Merbein Seedless (4.33) recorded maximum. The interaction effect on drying ratio between pre-treatment and varieties was not significant. Thompson Seedless variety showed lowest drying ratio which might be due to high total soluble solids and sugars accumulation in fresh berries as reported by Christensen and Peacock (2000). Jadhav *et al.*, (2010) also found that, pre-drying with 1.5% olive oil + 6% K₂CO₃ for 3 min. dipping at 42°C recorded the lowest dehydration ratio in Thompson Seedless grapes.

Drying time (days)

It was evident from table 1, significantly lowest drying time of 14.21 days was recorded in AEEO + AA 1000 ppm (A₃), whereas it was maximum in control (15.17 days), which might be due to high water loss (Figure 1) in present study. The time required for drying was lowest in AEEO either with AA or BA irrespective of their concentration compared with control. Regarding varieties,

Merbein Seedless berries dried quicker (13.64 days) and Sonaka takes more time (14.99 days) for drying (Figure 2). The drying time of Manik Chaman (14.85 days) and Thompson seedless (14.80 days) were comparable with each other. The shortest drying time was recorded in Merbein Seedless followed by 2A Clone, Thompson Seedless, Manik Chaman and Sonaka in order due to various rate of drying (Figure 2) in this study. The interaction effect on drying time between pre-treatment and varieties are not significant.

Average raisin weight (g)

Significantly the highest raisin weight was noted in pre-treatment A₃ (0.474 g) whereas it was lowest recorded in untreated berries (0.463 g). It was observed that there was no significant difference among the various concentrations of AA (500, 750 and 1000 ppm) as well as BA (50, 100 and 150 ppm) with AEEO as a pre-treatment on average raisin weight. Sonaka raisin recorded a maximum of 0.504 g, which was on par with Manik Chaman (0.501 g) whereas it was lowest in variety Merbein Seedless (0.426 g) in the present study could be due to the high moisture content in raisins (Ramming, 2009).

The interaction between pre-treatment and varieties was not significant. In our study the highest raisin weight was recorded in pre-drying treatment AEEO + AA 1000 ppm (A₃) which may be due to highest water loss (Figure 1) in the berries during drying period, which leads to higher raisin weight (Figure 1). Adsule *et al.*, (2008) also reported that the raisins prepared by dipping oil method in seedless grape varieties recorded raisin weight from 0.34 to 0.45 g.

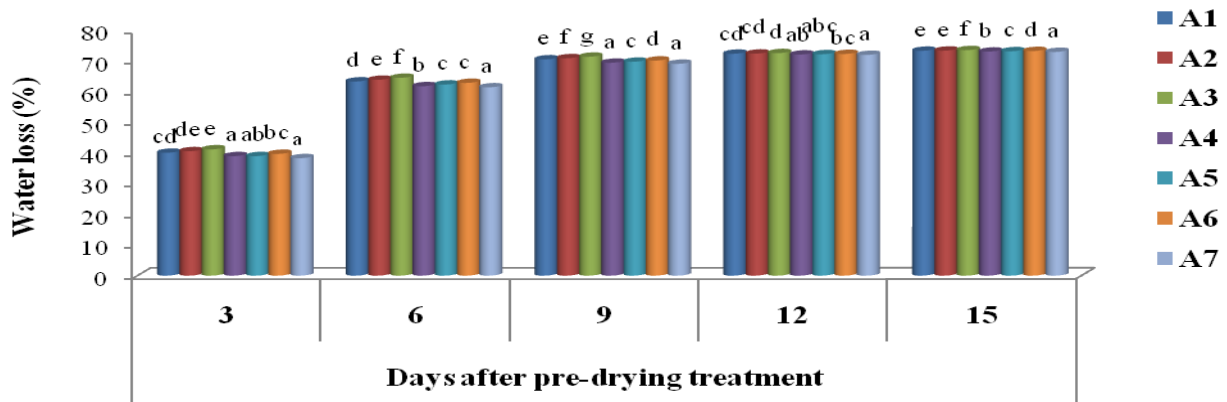
Raisin yield (kg/vine)

It was evident from data, there was significant difference (p=0.05) found among the treatments and varieties on raisin yield. The

maximum and on par raisin yield was recorded in A₃ (4.81 kg/vine), A₂ (4.71 kg/vine) and A₁ (4.70 kg/vine). The highest raisin yield was recorded in pre-drying treatment A_{EEO} + AA 1000 ppm (A₃) which may be due to the lowest raisin waste and highest average raisin weight (Table 1) was recorded in this treatment because the ascorbic acid play major role to terminate radical chain reactions ultimately leads to

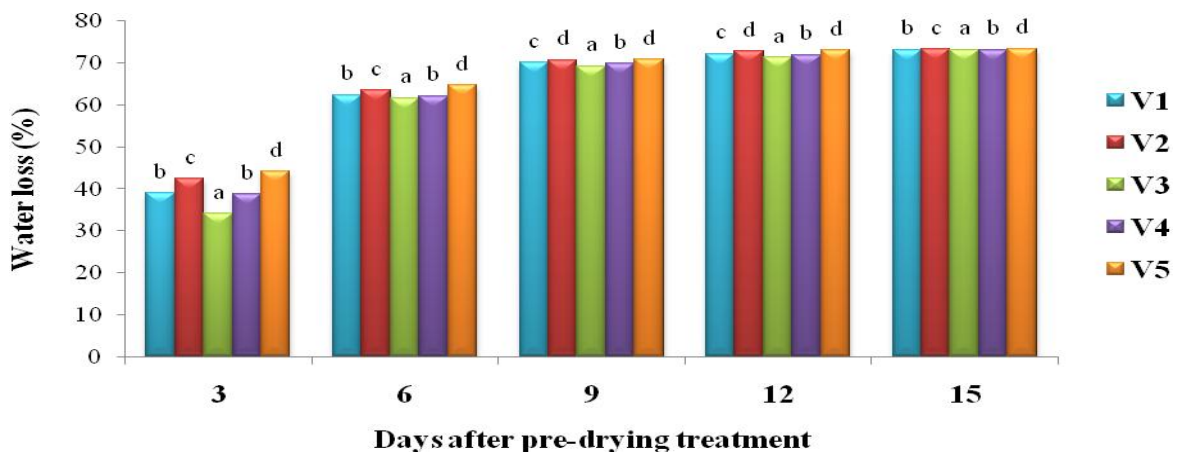
higher raisin yield (Davey *et al.*, 2000 and Farouk, 2011). The yield was recorded maximum in Thompson Seedless which might be due to its high total soluble solids and sugars in fresh berries corresponding increase in raisin yield. Obviously, Winkler (1962) and Jadhav *et al.*, (2010) also reported that greater the rate of sugars in fresh grapes, greater will be the raisin yield, which may be relatively the same for present studied varieties.

Fig.1 Rate of drying (per cent water loss during drying period) of grapes as affected by various concentrations of antioxidants with alkaline emulsion of ethyl oleate as a pre-drying treatment



Bars labelled with the same alphabets on each days after pre-drying treatment were not significantly different at $p \leq 0.05$.

Fig.2 Rate of drying (per cent water loss during drying period) of seedless grape varieties after pre-drying treatment



Bars labelled with the same alphabets within varieties on each day after pre-drying treatment were not significantly different at $p \leq 0.05$.

Table.1 Effect of various concentrations of antioxidants with alkaline emulsion of ethyl oleate (AEEO) as a pre-drying treatment on drying time, drying ratio (fresh grape to raisin), average raisin weight, raisin yield, raisins wastes and percentage of green, brown and mixed colored raisins prepared from seedless varieties of grapes

Pre-drying treatments (A)	Drying time (days)	Drying ratio (grape to raisin)	Average raisin weight (g)	Raisin yield (kg/vine)	Raisin wastes (g)	Percentage of colored raisins		
						Green	Brown	Mixed
A ₁ – AEEO + AA 500 ppm	14.34 ^{ab}	4.09 ^b	0.470 ^{ab}	4.70 ^{ab}	102.50 ^{bc}	70.52 ^b	9.78 ^{ab}	19.70 ^b
A ₂ – AEEO + AA 750 ppm	14.27 ^{ab}	4.07 ^{ab}	0.473 ^a	4.71 ^{ab}	100.90 ^{ab}	71.05 ^b	9.62 ^{ab}	19.33 ^{ab}
A ₃ – AEEO + AA 1000 ppm	14.21 ^a	3.99 ^a	0.474 ^a	4.81 ^a	99.30 ^a	72.28 ^a	8.64 ^a	19.08 ^a
A ₄ – AEEO + BA 50 ppm	14.47 ^b	4.15 ^b	0.467 ^{bc}	4.59 ^{bc}	105.05 ^{de}	67.70 ^d	10.62 ^b	21.68 ^d
A ₅ – AEEO + BA 100 ppm	14.44 ^b	4.14 ^b	0.467 ^{bc}	4.60 ^{bc}	103.60 ^{cd}	68.27 ^{cd}	10.22 ^b	21.51 ^{cd}
A ₆ – AEEO + BA 150 ppm	14.36 ^b	4.11 ^b	0.469 ^{ab}	4.61 ^{bc}	103.10 ^c	69.00 ^c	9.84 ^{ab}	21.16 ^c
A ₇ – AEEO (Control)	15.17 ^c	4.18 ^c	0.463 ^c	4.56 ^c	106.40 ^e	33.86 ^e	26.31 ^c	39.82 ^e
S.Em±	0.05	0.03	0.002	0.05	0.66	0.31	0.43	0.15
CD at 5%	0.14	0.08	0.005	0.15	1.86	0.91	1.23	0.45
Varieties (V)								
V ₁ – Thompson Seedless	14.80 ^c	3.87 ^a	0.465 ^b	5.30 ^a	99.24 ^a	67.58 ^a	11.40 ^a	21.02 ^a
V ₂ – 2A Clone	14.00 ^b	4.16 ^c	0.449 ^c	4.52 ^d	105.24 ^d	64.06 ^b	12.28 ^{ab}	23.66 ^b
V ₃ – Sonaka	14.99 ^d	4.10 ^c	0.504 ^a	4.73 ^c	102.69 ^c	61.18 ^d	13.15 ^b	25.68 ^d
V ₄ – Manik Chaman	14.85 ^c	4.02 ^b	0.501 ^a	5.09 ^b	100.90 ^b	67.39 ^a	11.35 ^a	21.27 ^a
V ₅ – Merbein Seedless	13.64 ^a	4.33 ^d	0.426 ^d	3.65 ^e	106.84 ^e	63.13 ^c	12.57 ^b	24.30 ^c
S.Em±	0.04	0.02	0.004	0.04	0.56	0.26	0.36	0.13
CD at 5%	0.12	0.07	0.001	0.13	1.57	0.76	1.04	0.38
Interactions (A x V)	NS	NS	NS	NS	NS	NS	NS	NS

Figures with different alphabet within pre-drying treatments (A) and varieties (V) are significantly different at p≤0.05; NS–Not significant.

AA – Ascorbic acid

BA – Benzyl adenine

Raisin wastes (g)

The raisin wastes (grams decayed raisins from 3 kg of fresh grapes) was recorded to be lowest in pre-drying treatment AEEO + AA 1000 ppm (A₃) which may be due to the ascorbic acid play major role to terminate radical chain reactions and protect tissue from damage ultimately leads to maximum yield and minimum wastes of raisins (Farouk, 2011). It was recorded lowest in variety Thompson Seedless than others in the present investigation which might be due to cultivar differences in berry cuticle and skin (Christensen and Peacock, 2000). The interaction effect was not significant with respect to raisin wastes (Table 1).

Percentage of colored raisins

Raisin color is one of the important qualitative aspects and plays an important role in consumer acceptance. Effect of various concentrations of antioxidants with AEEO as a pre-drying treatment on percentage of green, brown and mixed colored raisins prepared from seedless varieties of grapes are presented in table 1. Significant difference was observed among the pre-drying treatments and varieties on percentage of colored raisins (green, brown and mixed).

Percentage of green colored raisins

It was recorded to be higher in AEEO with AA or BA irrespective of their concentration compared with control (*i.e.* AEEO only). The percentage of green colored raisins increased with the increased concentrations of AA and BA (Table 1) and significantly highest percentage was recorded in A₃ (72.28%) and lowest in control (33.86%). There was significant difference found among the seedless grape varieties used for raisin making. Significantly higher percentage of green colored raisins was noted in Thompson

seedless (67.58%) which was on par with Manik Chaman (67.39%) and lowest in Sonaka (61.18%).

Percentage of brown colored raisins

The percentage brown colored raisins was observed lowest in pre-treatment AEEO with AA or BA irrespective of their concentration compared to control. Significantly lowest percentage was recorded in Manik Chaman (11.35%) which was comparable with Thompson seedless (11.40%) and 2A Clone (12.28%) whereas highest percentage was found in Sonaka (13.15%), which was on par with Merbein Seedless (12.57%) and 2A Clone (12.28%).

Percentage of mixed colored raisins

It was evident from table 1, that the percentage mixed colored raisins are significantly influenced by various concentrations of antioxidants with AEEO as well as varieties and lowest recorded in A₃ (19.08%) which was on par with A₂ (19.33%) whereas highest in control (39.82%). It decreased with the increase of both AA and BA concentrations with AEEO. The variety Thompson Seedless (21.02%) recorded lowest percentage of mixed colored raisins which was on par with Manik Chaman (21.27%) and maximum percentage was noted in Sonaka (25.68%). The interaction effect on percentage of green, brown and mixed colored raisins between various concentrations of antioxidants with AEEO and varieties were not significant.

The pre-drying treatment of grapes with AEEO either with AA and BA effectively reduces brown and mixed colored raisins and correspondingly elevates green colored raisins (Table 1) compared to control due to inhibition of polyphenol oxidase activity (Zhang Yu, 2008). AEEO with AA 1000 ppm

(A₃) pre-drying treatment was most effective because the ascorbic acid acts more as an antioxidant than as an enzyme inhibitor due to it reduces browning reactions (Smirnoff, 2000; Rapeanu *et al.*, 2006; Farouk, 2011 and Kendall and Sofos, 2012). Ascorbic acid spray after AEEO (1.5% EO + 2.5% K₂CO₃) pre-treatment minimizes browning and to elevate the overall acceptability in raisins (Sharma *et al.*, 2012). Regarding varieties, Thompson Seedless and Manik Chaman shows the best results with respect to percentage of raisin color might be due to fruits may show large difference in their tendency to brown because of cultivar variation in polyphenol oxidase activity as reported by Sapers and Hicks (1993).

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