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Biochemical characterization of raisin varieties grown under semi-arid condition

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Abstract

Fifteen different grape varieties were evaluated for raisin making and raisin quality. The highest raisin recovery was observed in Clone 2A as compared to other varieties in this study. Amongst the different varieties, TSS ranged from 22.30 °B in AH-2-8 to Manjari Kishmish and Clone 2A with 23.60 °B TSS. The highest reducing sugar content in fresh berries and raisins was recorded in Rieber variety. The highest protein content in fresh berries and raisin was recorded in Sundekhani and Merbein Seeded. However, the highest phenol concentration was found in Manjari Kishmish and Convert Large Black. The maximum carbohydrate was higher in Red Muscat and Athens. The variety Clone 2A was found better for higher raisin recovery and can be a potential variety in grape growing regions for raisin purposes.

Key words: *Vitis vinifera,* TSS, variety, raisin recovery, carbohydrate

Introduction

Grape (*Vitis vinifera* L.) is one of the major important commercial fruit crops grown in India. Basically, it is a temperate crop that has been successfully adopted to the sub-tropical as well as tropical climate and is well known for its various health benefits. The cultivated area under grape is approximately 1.62 lakh ha resulting an annual production of 34.45 lakh MT with an average productivity of 21.00 MT/ha (Anonymous, 2023). In India, a production of 2.8 lakhs of raisins was estimated in 2019 from the grape drying areas of Sangali, Solapur and Nashik in Maharashtra and Vijayapura and Bagalkot in Karnataka (Sharma *et al.,* 2020). About 90% production of Maharashtra are primarily used for raisin making by using Thompson Seedless or its clonal like Tas-A-Ganesh and Sonaka (Somkuwar *et al.,* 2019). This is because seedless raisin varieties have higher phenolic compound, vitamin, and mineral content, as well as higher antioxidant capacity compared to seeded varieties (Kaya *et al.*, 2022). The sugar content in grape berries at the time of harvesting also plays a significant role in raisin recovery, in addition to the total yield (Sharma *et al.,* 2018). The grape harvesting dates also impact the yield, color, and quality of raisins, with well-matured grapes resulting in fewer brown and mixed-colored raisins and an increase in green-colored ones in Thompson Seedless or its clonal selections (Venkatram *et al.,* 2020). Physical characteristics, chemical composition, and optimization of drying and pre-treatment operations are responsible for quality of raisins (Khiari *et al.,* 2018). Both grapes and raisins have a significant role in the food industry and offer numerous health benefits when included in the diet. Raisins, being dried grapes, inherit all the benefits of grapes and offer additional advantages such as longer shelf life and concentrated nutrients. Variability was recorded in bunch, berry, and raisin parameters across the various varieties. The overall performance of varieties under conditions decide further adaptability by the grape growers. Besides the total yield, the sugar content of the grape berries at the time of harvesting also plays a major role in raisin recovery (Sharma *et al.,* 2018). In the raisin industry, the variety which can produce good yield with a high potential of raisin recovery has a bright future.

Drying grapes into a raisin is a common processing method in all grape growing regions. Traditionally, raisins are made by sun drying grapes for 8-10 days, which significantly reduces their water content. Raisins (dried grapes) are popular in the mediterranean region and are widely used as a traditional and natural biomedicine in several countries (Cordero-Bueso *et al.*, 2017). It is also been a favorite food due to nutritive value and high micronutrients content (Ghrairi *et al.,* 2013). The phenolic acids and flavonoids found in raisin, such as benzoic and hydroxycinnamic acids, resveratrol, flavan-3-ols, catechin, and epicatechin, and flavanols, such as kaempferol, quercetin, myricetin, and anthocyanins, are closely related to antioxidant activity. The nutritional and phytochemical properties e.g., carotenoids, phenolic acids, flavonoids, phytoestrogens, and anthocyanins of many dried fruits have been extensively studied by Benlloch-Tinoco *et al.* (2015) and Chang *et al.* (2016).

The quality of dried grapes is affected by growing conditions and adopted processing methodologies. It is well proven that colored seeded grapes have more health benefits. Among the table grape varieties, Thompson Seedless or its clones are mainly used for raisin making worldwide. The quality attributes directly related to human health also play an important role in deciding the verities for this purpose. It is well proven that raisins are not only a good source of essential vitamins and minerals but they are also cholesterol and fat-free, rich in antioxidants, and dietary fibers and contain 70% fructose that is easy to digest (Witherspoon, 2000;

Sanz *et al.,* 2001). The demand for black raisins is increasing very fast as these are being used in the preparation of various types of medicines besides wide utilization in bakery and dairy products. Consumers are much more aware of healthy foods and want to take black raisins as snacks also. Hence, considering the demand for different grape varieties for quality raisins, the present study was conducted.

Material and Methods

The experiment was carried out in the experimental vineyards of ICAR-National Research Centre for Grapes, Pune during the year 2022-23. The experimental site is in mid-western Maharashtra, India ($18^0$32'N and $73^0$51'E). Vines frafted on Dogridge rootstock (trained on Y trellises) were selected for the study. Vines were spaced 10 feet between the rows and 6 feet between vines, thus accommodating 726 vines per acre. Under tropical conditions, the vines were pruned twice a year. The first pruning was done in April (foundation pruning) while the second pruning was done in October (fruit pruning). All the standard recommended cultural practices for the region were followed during the period of study.

Quality parameter: The total soluble solids (TSS) and titratable acidity (TA) in the berries were estimated by extracting juice from crushed berries (about 50 berries randomly collected from different vines of the same replication) and then centrifuged at 5000 rpm for 5 minutes. The data were recorded using an FTIR based wine analyzer (OenoFoss) and expressed in °Brix and g/L. The grape juice was extracted and the total soluble solid was recorded using a refractometer (Erma, Japan) while the acidity was measured using a titration method. One kg fresh grapes were dipped in emulsion of 2.5% potassium carbonate and 1.5% ethyl oleate for 10 minutes and subsequently dried under raisin shade for 12-14 days. When the moisture content of dried grapes (raisins) reached to 16%, final weight was recorded, and raisin recovery was calculated using the formula:

Raisin recovery = weight of raisins/weight of fresh grapes x 100.

Biochemical composition parameters: To estimate the biochemical, dinitrosalicylic acid (DNSA) method was used to estimate reducing sugar while, protein estimation was done by Lowry *et al.* (1951) method and was expressed in mg g^{-1}. The phenols were determined by Folin-Ciocalteu method as suggested by Singleton (1965) using gallic acid as standard and was expressed in mg g^{-1}, while total carbohydrate was estimated using Anthrone method with D-glucose as the standard (Sadasivam and Manickam, 1997).

Statistical analysis: The experiment was conducted in a randomized block design with fifteen varieties as treatments replicated three times. The data recorded on various parameters were statistically analyzed and tabulated using means of each treatment. The analysis of data was performed by using SAS version 9.3.

Results and discussions

Quality parameters: Total soluble solid is an important parameter considered for raisin recovery. The higher the TSS, the higher will be the raisin recovery. Among the different accessions, TSS ranged from 22.30 °B to 23.60 °B. The variety Manjari Kishmish and 2A Clone exhibited higher TSS (23.60 °B) which was at par with Ribier (23.40 °B) while AH-2-8 recorded the lowest TSS (22.30 °B). The TSS in all the studied varieties was above the standard values as reported by McCoy *et al.* (2015) in Afghan raisins. Somkuwar *et al.* (2020) revealed that the grape types affect raisin quality as every grape type has its features like berry size, titratable acidity (TA), total soluble solids, etc. and it reflects in the quality of the dried grapes. The acidity was low in Kishmish Belyi, AH-2-8 and Convert Large Black (5.50 g/L) followed by Athens (5.80 g/L) and Thompson Seedless (5.90 g/L) while the variety Black Prince exhibited higher acidity of 6.52 g/L. Apart from those mentioned above, the other varieties exhibited acidity in the range of 5.50 to 6.52 g/L. Barnuud *et al.* (2014) also found that berries from warmer regions had low levels of titratable acidity and high pH compared to berries from the cooler regions at a common maturity of 22 °Brix. Similar trend for TSS and titratable acidity were also reported by Somkuwar *et al.* (2023). Highest raisin recovery was observed in 2A Clone (27.40%) which was at par with Convert Large Black (26.90%) and Kishmish Belyi (26.85%) while lowest raisin recovery was recorded in Athens (22.20%). Fruit characteristics play an important role in raisin quality. Somkuwar *et al.* (2020) also found that fresh grapes with the highest sugar levels resulted in high raisin recovery. Selecting grapes with higher sugar levels (Brix of 20% more) results in higher raisin recovery rates and superior quality, appearance, and taste.

Table 1. Evaluation of grape varieties for quality parameters

Variety	TSS (°Brix)	TA (g/L)	Raisin recovery (%)
Ribier	23.40^{ab}	6.30^{bc}	25.70^{d}
Black Monukka	22.60^{c}	6.30^{bc}	26.10^{cd}
Manjari Kishmish	23.60^{a}	6.42^{ab}	26.60^{bc}
Kishmish Rosavis	22.80^{c}	6.30^{bc}	24.70^{e}
Merbein Seedless	22.40^{c}	6.20^{cd}	25.75^{d}
Sundekhani	22.70^{c}	6.50^{a}	24.25^{e}
Thompson Seedless	22.65^{c}	5.90^{e}	25.70^{d}
2A Clone	23.60^{a}	6.30^{bc}	27.40^{a}
Kishmish Belyi	22.72^{c}	5.50^{f}	26.85^{ab}
AH-2-8	22.30^{c}	5.50^{f}	25.65^{d}
Convert Large Black	22.50^{c}	5.50^{f}	26.90^{ab}
Athens	22.80^{c}	5.80^{e}	22.20^{f}
Black Prince	22.60^{c}	6.52^{a}	26.50^{bc}
Carolina Black Rose	22.82^{c}	6.10^{d}	24.60^{e}
Red Muscat	22.84^{bc}	6.30^{bc}	24.35^{e}
SEm±	0.20	0.06	0.23
CD 5 %	0.57	0.17	0.65

Significant at $P < 0.05$

Biochemical composition of grape berries and raisin: The data on biochemical constituents in fresh berries and raisins made from different varieties are presented in (Table 2). In fresh grape berries and raisin, the highest reducing sugar content was estimated in Riber (19.35 and 44.20 mg/gm) while the lowest reducing sugar was recorded in Merbein Seedless (16.90 mg/g) in fresh berries and raisins of AH-2-8 (37.40 mg/gm). The maximum protein content was recorded in Sundekhani and Merbein Seedless (2.50 and 44.35 mg/gm, respectively) in fresh grape and raisins, while minimum protein was recorded in Kishmish Belyi and Ribier (1.03 and 35.15 mg/gm) in fresh berries and raisins. Somkuwar *et al.* (2013) observed maximum protein content in raisin (28.50 mg/g) as compared to fresh grape (5.60 mg/g) in Thompson Seedless. Grape composition changes during the drying process, particularly with an increase in sugar concentration might be due to grape dehydration (Franco *et al.,* 2024). In the earlier studies, Satisha *et al.* (2014) also reported increase in protein content and reducing sugar while reduction in phenolic concentration in raisin compared to fresh grapes of Thompson Seedless grafted on different rootstocks. The highest phenol concentration was found in Manjari Kishmish and Convert Large Black (4.52 and 1.56 mg/g, respectively) while lowest in Merbein Seedless (2.45 and 0.88 mg/g) in fresh berries and raisins. Similar results were also obtained by Shao *et al.* (2016) where large variations in phenolic compounds and their contents among different raisins were reported. The result of present study also confirms with the findings of Somkuwar *et al.* (2020) who reported 0.12 to 1.64 mg/g phenol content in raisin. Significant differences were observed in varieties for carbohydrates. In fresh grape and raisins, Red Muscat and Athens variety had highest carbohydrate level (267.40 and 787.37 mg/gm), while lowest carbohydrate was observed in Ribier and Convert Large Black (225.00 and 624.17 mg/gm, respectively). Somkuwar *et al.* (2013) reported that preparation of raisin from fresh grape is the process of drying in which berries loose water which helps in accumulating the carbohydrate in berries.

Table 2. Evaluation of grape varieties for biochemical composition in fresh berries and raisins

Variety	Reducing Sugar (mg/g)		Protein (mg/g)		Phenol (mg/g)		Total Carbohydrate (mg/g)	
	Fresh	Dried	Fresh	Dried	Fresh	Dried	Fresh	Dried
Ribier	19.35	44.20	1.61	35.15	4.10	1.07	225.00	649.97
Black Monukka	17.52	43.50	1.58	39.20	3.54	1.07	265.70	734.92
Manjari Kishmish	17.35	43.21	1.55	45.35	4.52	1.13	245.50	785.79
Kishmish Rosavis	17.58	39.85	1.94	41.28	3.65	1.25	265.80	723.77
Merbein Seedless	16.90	41.50	1.57	44.35	2.45	0.88	255.80	774.87
Sundekhani	18.64	40.21	2.50	40.15	2.86	0.93	260.40	711.90
Thompson Seedless	19.20	41.00	2.14	39.40	3.45	1.05	265.60	734.92
2A Clone	19.10	38.50	1.94	41.44	3.44	1.03	250.50	753.92
Kishmish Belyi	17.65	38.45	1.03	45.25	3.87	1.17	264.40	680.02
AH-2-8	17.20	37.40	1.42	37.85	3.95	1.19	235.40	646.23
Convert Large Black	18.10	43.50	1.68	38.25	3.20	1.56	245.20	624.17
Athens	18.00	42.47	1.75	39.10	3.15	1.09	256.30	787.37
Black Prince	19.15	41.65	2.00	38.60	3.30	1.09	240.50	663.90
Carolina Black Rose	18.32	43.55	2.15	37.50	4.12	1.48	235.50	625.56
Red Muscat	18.55	43.90	1.95	43.50	2.90	1.23	267.40	677.92
SEm±	0.16	0.35	0.02	0.38	0.03	0.01	2.11	7.01
CD 5 %	0.46	1.02	0.06	1.09	0.10	0.02	6.11	20.30

Correlation among the quality and biochemical composition traits: To study the relationship between quality and biochemical composition traits among the varieties, a correlation analysis was carried out (Table 3). The present study revealed that TSS has a moderate positive correlation with titratable acidity (0.463) and total carbohydrate (0.285). The positive correlation between TSS and TA suggests that higher sugar content might also increase the acidity, which could affect the overall taste profile. The pH has a strong positive correlation with total carbohydrate (0.616), suggests that change in pH levels could influence the carbohydrate composition, impacting the sweetness and nutritional value. Titratable acidity has moderate correlations with TSS (0.463) and reducing sugar (0.550). This implies that higher acidity in the varieties is associated with higher TSS and reducing sugar content. Raisin recovery has weaker correlations with other variables, suggesting that it might be influenced by factors not strongly related to the biochemical traits measured in this study. Reducing sugar has positively correlated with TA (0.550) and a negatively correlated with pH (-0.354). Protein has moderate correlations with total carbohydrate (0.529). Phenol has a moderate negative correlation with total carbohydrate (-0.650). The results of the present study are indicating that higher phenol content is associated with lower carbohydrate content. Total carbohydrate has strong positive correlations with pH (0.616) and protein (0.529). It has a strong negative correlation with phenol (-0.650).

Table 3. Simple correlation among quality and biochemical composition variable utilized for the studied raisin cultivars

Trait	TSS (°Brix)	pH	TA (g/L)	Raisin recovery (%)	Reducing sugar (mg/g)	Protein (mg/g)	Phenol (mg/g)
TSS (°Brix)	1						
pH	0.126	1					
TA (g/L)	0.463	0.084	1				
Raisin recovery (%)	0.310	0.057	-0.155	1			
Reducing sugar (mg/g)	0.154	-0.354	0.550	-0.181	1		
Protein (mg/g)	0.153	0.238	-0.056	0.127	-0.217	1	
Phenol (mg/g)	-0.134	-0.337	-0.148	0.035	0.269	-0.251	1
Total carbohydrate (mg/g)	0.285	0.616	0.263	-0.160	-0.086	0.529	-0.650

Fifteen raisins grape cultivars were studied for their biochemical composition, individual phenolic and flavonoid content. Varietal behaviour under tropical conditions has been evaluated along with quality of raisin. A significant difference was observed for quality parameter of grape. Grapes are rich in phenolic compound as compared to raisin. The 2A Clone had highest raisin recovery. In term of varietal evaluation based on biochemical constitutes, Rieber exhibited the highest reducing sugar content, while Sundekhani and Merbein Seedless had the highest protein content. The highest phenol content was found in Manjari Kishmish and Convert Large Black, while the carbohydrate was observed in Red Muscat and Athens.

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