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PHYSIOCHEMICAL AND MINERAL CHARACTERIZATION OF UNEXPLORED LOCAL GRAPES (*Vitis vinifera* L.) CULTIVARS GROWING IN BALOCHISTAN PROVINCE, PAKISTAN

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ABSTRACT

Grapes (*Vitis vinifera* L.) are highly valuable crops enriched with minerals, vitamins, phenolics, and antioxidants required for daily human activities and to prevent cancer and cardiovascular diseases. The objective of this study was to elucidate the physicochemical and mineral evaluation of seven neglected local grape cultivars ('Kishmish', 'Sra Kishmish', 'Askari', 'Sahibi', 'Haita', 'Sundar Khani' and 'Toran') growing in Baluchistan, as it can help in future breeding, processing, and species conservation. Therefore, these cultivars were evaluated for different physical, biochemical, and availability of macro– and micro–mineral contents. In physical evaluation, the local cultivar 'Haita' showed maximum bunch length (19.72 cm) and bunch width (11.88 cm), while the highest bunch weight (527.33 g) was recorded in 'Sahibi'. Similarly, significant differences were noted in biochemical traits, and maximum total soluble solids (24.76%) and titratable acidity (1.58%) were observed in 'Sundar Khani', while the highest vitamin C (26.17 mg 100 g^{-1}), total sugars (30.26%) in Sundar Khani, and nonreducing sugars (8.79%) were recorded in 'Haita'. The cultivars growing in Balochistan also showed variations in phenolics (113.79–346.50 mg GAE L^{-1}) and antioxidants (85.77–90.87%). Likewise, the concentrations of macro- and microelements were also highly variable in these cultivars. Overall, among these cultivars, 'Toran' performed better in the agroclimatic conditions of Balochistan, as it has high yield attributes such as berry length, width, and weight. Moreover, it was also enriched with total soluble solids, antioxidants, and calcium contents.

Key words: antioxidants, microelements, local cultivars, minerals, phenolics

INTRODUCTION

Grape (*Vitis Vinifera* L.) belongs to the family Vitaceae and is cultivated worldwide on an area of 7.3 million hectares with a production of 85 million tons, of which 57% is used to make wine, 36% is consumed fresh as table grapes, and the remaining 7% is dried for raisins [Office International de la Vigne et du Vin. 2019]. Grapes are enriched in genetic diversity and globally have more than 10,000 cultivars

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[Teixeira et al. 2013]. In Pakistan, grapes are grown on 15,000 hectares, yielding approximately 643 thousand tonnes. More than 70% of grapes are grown in the province of Balochistan districts (Quetta, Kalat, Loralai, Pisin, Killa Saifullah, Chagai, Zhob, and Mastung). In contrast, the remaining grapes are produced in Khyber Pakhunkhwa districts (Bajoure, Chitral, Charsadda, Nowshera, and Orakzai) and Punjab (especially in northern areas) [Akram et al. 2019]. Due to the ideal temperature for early mature cultivars, it is also becoming well known in subtropical areas of Punjab, usually in the Potohar range. In Pakistan, only European grapes, known as table grapes, are grown and utilized as fresh raisins and in beverage industries for juices.

Grapes are highly nutritious and enriched with sugars, vitamins, and organic acids required for the normal functioning of body organs [Mikulic et al. 2019, Hegedus et al. 2010]. In addition, grapes contain flavonoids, phenols, and antioxidants with anticancer, antiaging, antibacterial, and anti-inflammatory properties and protect against cardiac disorders [Mattivi et al. 2009, Lorrain et al. 2011, Sabra et al. 2021]. Likewise, minerals play an essential role in regulating certain metabolic functions and respond as catalysts for different enzymes by maintaining the balance in the acid-base ratio and osmotic pressure, facilitating the movement of vital materials through the membranes [Ali and Deokule 2009, Weyh et al. 2022]. The human body requires a particular amount of these minerals in its daily diet, as they cannot synthesize naturally [Onianwa et al. 2001, Jaiswal et al. 2022]. Generally, macrominerals are required in larger quantities higher than 100 mg/day, while humans require microelements in smaller amounts lower than 100 mg/day for normal body functions [Murray et al. 2000, Affonfere et al. 2021]. Grape is a blessed fruit enriched with macro- and microminerals that maintain blood pH and strengthen bones and teeth [Keskin et al. 2019]. The amounts of minerals and other grape berry constituents vary with soil type, cultural practices, climatic factors, and cultivars [Martins et al. 2012]. This variation is necessary among genotypes to improve the traits of existing varieties and for breeding new varieties [Riaz et al. 2018, Akram et al. 2019].

Baluchistan is rich in natural flora, and various temperate fruits are widely grown in this region. Despite being the center of diversity for many fruit crops, it is still an unexplored area. There are abundant local and wild grape genotypes present in upland areas of this region that are still unexplored, with little research work done. Moreover, this area is neglected and has fewer resources than other provinces. The availability of reliable information is essential for germplasm preservation, variety development, and breeding programs. In grapes, genotypes are distinguished on morphological, genetic, and biochemical traits for species conservation, identification, and duplicate detection [Khawale and Singh 2005, Ates et al. 2011, Leao et al. 2011, Fahmi et al. 2012, Akram et al. 2019]. Regardless of the high production of grapes in Baluchistan, there is no data available on grape physiochemical and mineral characterization, and several homonym and synonym cases of grapes are present in this area. Furthermore, farmers' preference for specific cultivars is disappearing for local cultivars. Therefore, this study aims to characterize local and exotic grape cultivars growing in Baluchistan based on physical and biochemical characteristics for future breeding programs and germplasm conservation.

MATERIALS AND METHODS

This study was conducted during 2017–2018 on seven local grape commercial cultivars (Kishmish, Sra Kishmish, Askari, Sahibi, Haita, Sundarkhani, and Toran). A detailed description of these cultivars is presented in Table 1. The plants were selected from the grape germplasm unit maintained at the experimental farm of Quetta Agricultural Research Institute (ARI) Balochistan, Pakistan. The average humidity, precipitation, and temperature (minimum, maximum, and average) climatic data were recorded throughout the study period (Figs 1 and 2). All the plants were healthy and active at five years of age, and the cultural practices adopted for all cultivars were similar throughout the study period.

Physical traits. For physical traits, three plants of each cultivar were randomly selected, and two grapes were selected from each grapevine to ensure data productivity. After the grape bunches were transported through a well-ventilated vehicle to the Citrus Sanitation Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, several bunches

Table 1. Description of grape cultivars growing in Balochistan, Pakistan

Cultivars	Genitors/Species	VIVC number	Color of skin of the berries	Consumption/Usage
Toran	*Vitis vinifera* L. subsp. *vinifera*	40624	Dark red	Table, raisin and wine purposes
Kishmish	*Vitis vinifera* L. subsp. *vinifera*	42295	Yellow	Table and raisin purposes
Sundar Khani	*Vitis vinifera* L. subsp. *vinifera*	27328	Yellowish green	Table and raisin purposes
Askari	*Vitis vinifera* L. subsp. *vinifera*	17421	Light greenish	Table and raisin purposes
Haita	*Vitis vinifera* L. subsp. *vinifera*	5259	Yellowish green	Table and raisin purposes
Sra Kishmish	*Vitis vinifera* L. subsp. *vinifera*	–	Light purple	Table and raisin purposes
Sahibi	*Vitis vinifera* L. subsp. *vinifera*	42307	Light purple	Table use only

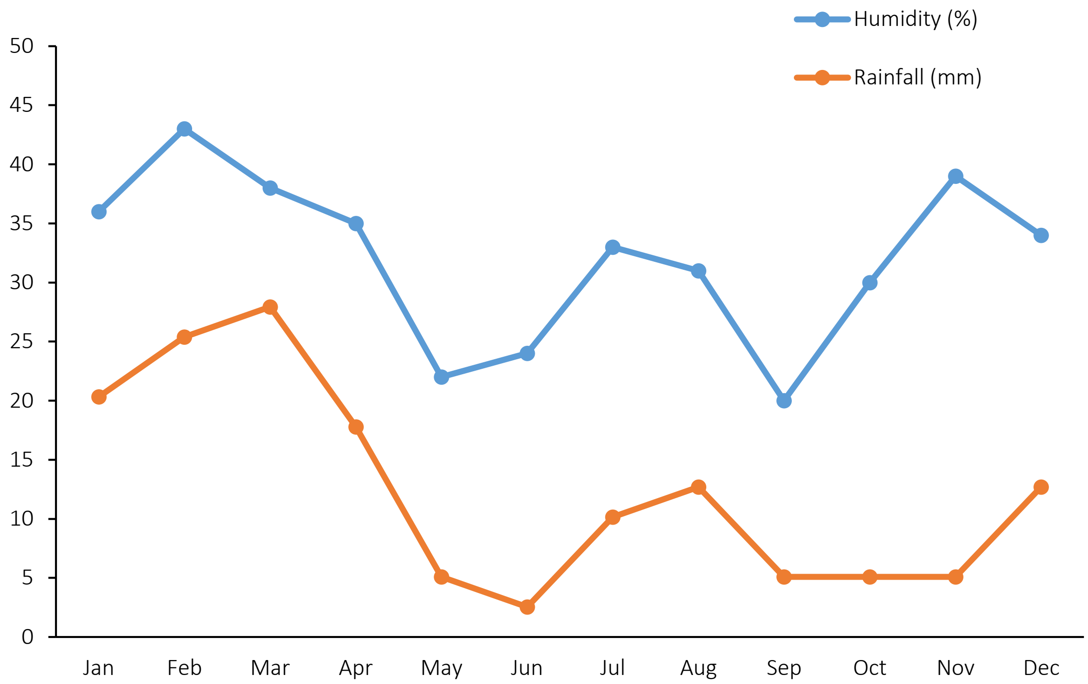

Fig. 1. The average humidity (%) and rainfall (mm) of Quetta, Pakistan, recorded from January to December 2018

and berry traits were noted. For bunch traits, bunch length (cm), bunch width (cm), rachis length (cm), peduncle length (cm), and bunch weight (g) was measured, while for berry parameters, the weight of ten berries (g), number of berries in a bunch, berry length (mm), berry width (mm), seed length (mm) and seed width (mm) were determined.

Biochemical analysis. For the biochemical analysis, grape berry juice was extracted with the help of a muslin cloth by twisting berries. A separate cloth was used for each replication, and hands were washed properly to avoid contamination. Different biochemical attributes, such as total soluble solids (TSS, °Bx), titratable acidity (TA, %), vitamin C (mg 100 g^{-1}), TSS: TA ratio, fruit juice pH, total sugars (TS, %), reducing sugars (RS, %) and nonreducing sugars (NRS, %), were determined.

TSS (°Bx) and TA (%). TSS was determined with the help of a hand refractometer (RS-5000 Atago, Japan) by placing a drop of grape juice under the mirror,

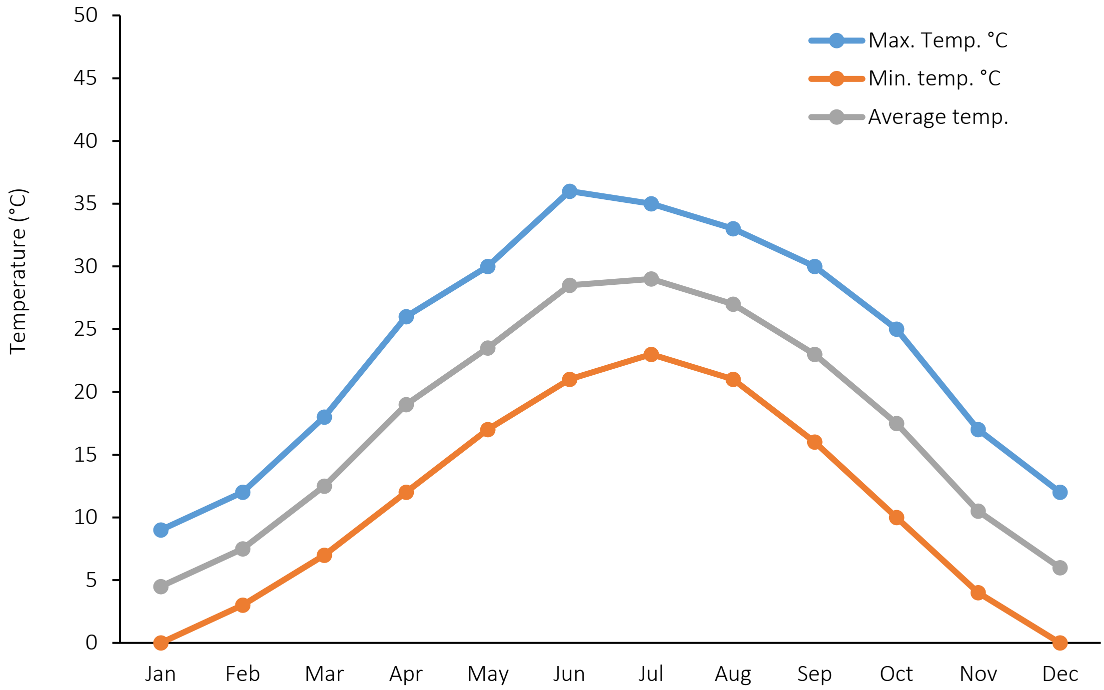

Fig. 2. **Fig. 2.** The minimum, maximum, and average temperatures (°C) of Quetta, Pakistan, recorded from January to December 2018

and the reading was determined in Brix. The titratable acidity was calculated by the following procedure described by [Hortwitz 1960]. This method diluted 10 mL of grape berry juice with 50 mL of distilled water and titrated it against 0.1 N NaOH. After two drops of phenolphthalein, as an indicator, were added to the solution to light pink color, its unit was expressed in percent (%).

Vitamin C (mg 100 g^{-1}), TSS: TA ratio, and pH. Vitamin C contents in grape berries were evaluated by the procedure mentioned by [Ruck 1969]. In this procedure, 10 mL of grape juice was placed in a 100 mL volumetric flask and diluted with 0.4% oxalic acid. In the next step, 5 mL of filtrated aliquot was taken and titrated against 2,6-dichlorophenolindophenol dye until light pink. A digital pH meter (HI 98107, Mauritius) was used to determine the pH value of grape juice. The meter tip was immersed in distilled water to neutralize it in this procedure. After the pH meter, the rod tip was inserted into grape juice samples, and the readings were noted.

Determination of sugars. All total sugars and reducing and nonreducing sugars in grape juices were measured by the following protocol defined by [Khan et al. 2008]. In this procedure, 10 mL of individual grape variety juice was diluted in 100 mL of distilled water, 10 mL of potassium oxalate (20%), and 25 mL of lead acetate (25%). The filtrate was used to calculate the number of various sugars (reducing, nonreducing and total sugars), and its unit was expressed in percent (%).

Total phenolic contents (GAE). Total phenolic contents were analyzed by the Folin-Ciocalteu (FC) method, as explained by Ainsworth and Gillespie [2007]. This method diluted 1 mL of grape juice in 9 mL of distilled water. After shaking, 1 mL of FC reagent was mixed thoroughly in a prepared solution. After that, the solution was allowed to settle for 5 min and supplemented with Na_2CO_3 (7%) solution. The ready solution was leveled to 25 ml with distilled water and then incubated for 2 h at room temperature. Then, 200 µl was taken with the help of a pipette and transferred to a 96-well plate, and the absorbance was measured at 765 nm with the help of a spectrophotometer. The TPC amount was calculated using the calibration curve for gallic acid. The total phenolic content results were expressed as gallic acid equivalent (GAE) juice.

Antioxidant activity (%). Total antioxidant activity was calculated by the procedure explained by [Brand-Williams et al. 1995]. In this method, grape juice (0.1 mL), DPPH radical solution (0.6 ml), and absolute ethanol (0.06 ml) were mixed and shaken vigorously. Then, the cells were placed in darkness for 30 minutes. Then, the prepared solution was placed in a ninety-six-well plate, and absorbance readings were taken with a UV-Vis spectrophotometer. A blank solution without a grape was run as a control to compare with readings. The following formula was used to measure the antioxidant activity in (%) percentage:

$$\text{Antioxidant activity (\%)} = [1 - (\text{sample 517 nm})] * 100$$

Determination of essential macro- and microelements: Different macro- [nitrogen (N), phosphorus (P), potassium (K), sodium (Na), calcium (Ca)] and microelements [zinc (Zn), iron (Fe), manganese (Mn), copper (Cu) and cobalt (Co)] were detected from different grape cultivar juices. For macroelements, N was estimated using the micro Kjeldahl method as described by [Chapman and Parker 1942]. This process was completed in two steps, including distillation and titration, and P was analyzed by the method of Chapman and Parker [1961], while K was determined using a flame photometer by the procedure followed by [Chapman and Parker 1961]. For the determination of Ca, Co, Cu, Fe, Mn, Na, and Zn from the digested sample, an atomic absorption spectrophotometer (Hitachi Polarized Zeeman AAS, Z-8200, Japan) was used. This procedure used standard solutions from the stock solution to prepare a calibration solution for atomic absorption spectrophotometer measurement according to the norm [Kacar and İnal 2008].

The units used to express N, P, K, and Na were percentages (%), while Ca, Zn, Fe, Mg, Cu, and Cb were expressed in mg L^{-1}.

Statistical analysis

Using statistical software 8.1, data were examined using analysis of variance (ANOVA). The design was completely randomized (CRD), and Tukey's HSD test was used to determine mean differences. A single grapevine was used as the experimental unit, and three uniform bunches were collected from individual grapevines with at least three replications. Therefore, there were three plants of individual cultivars with nine bunches. Hence, the mean of three bunches was taken as a single replicate. Pearson correlation was performed to check the relationship between the studied variables.

RESULTS

Morphological attributes

Bunch characteristics. All the grape cultivars exhibited significant variations in bunch characteristics (Fig. 3a). In our findings, the highest bunch length (19.72 cm) was observed in 'Haita', while the lowest bunch length (14.85 cm) was recorded in 'Toran'. Similarly, significant variations were noted in bunch width traits, ranging between 9.38 and 11.88 cm, and the maximum bunch width was observed in 'Haita', while the minimum bunch width was noted in 'Askari'. However, the maximum rachis length (44.01 cm) was recorded in 'Kishmish', and the minimum length (19.16 cm) was found in 'Toran'. The rachis length also varied with cultivar, and 'Toran' showed the highest peduncle length (4.33 cm), followed by 'Sahibi' (3.88 cm), while the shortest peduncle length was observed in 'Haita' (2.94 cm).

The other characteristics of bunch weight, the weight of ten berries, and the number of berries in a bunch are shown in Fig. 3b. The results depicted significant variations in these traits as well, and the maximum bunch weight (527.33 g) was recorded in 'Sahibi', followed by 'Toran' (454.66 g) and 'Haita' (431.0 g), whereas the minimum bunch weight (210.66 g) was noticed in 'Sundarkhani'. Likewise, a significant difference was also observed in the number of berries in a bunch, and the maximum number of berries per bunch was recorded in 'Askari' (154), while the lowest number of berries (93.66) was found in 'Sahibi'. Similarly, the highest weight of 10 berries was observed in 'Toran' (55.33 g), and the lowest berry weight was observed in 'Askari' (12.0 g).

Berry and seed traits. In Figure 3c, berry and seed traits are shown. The results revealed significant differences in these traits, and the maximum berry length (23.17 mm) was observed in 'Sahibi', while the

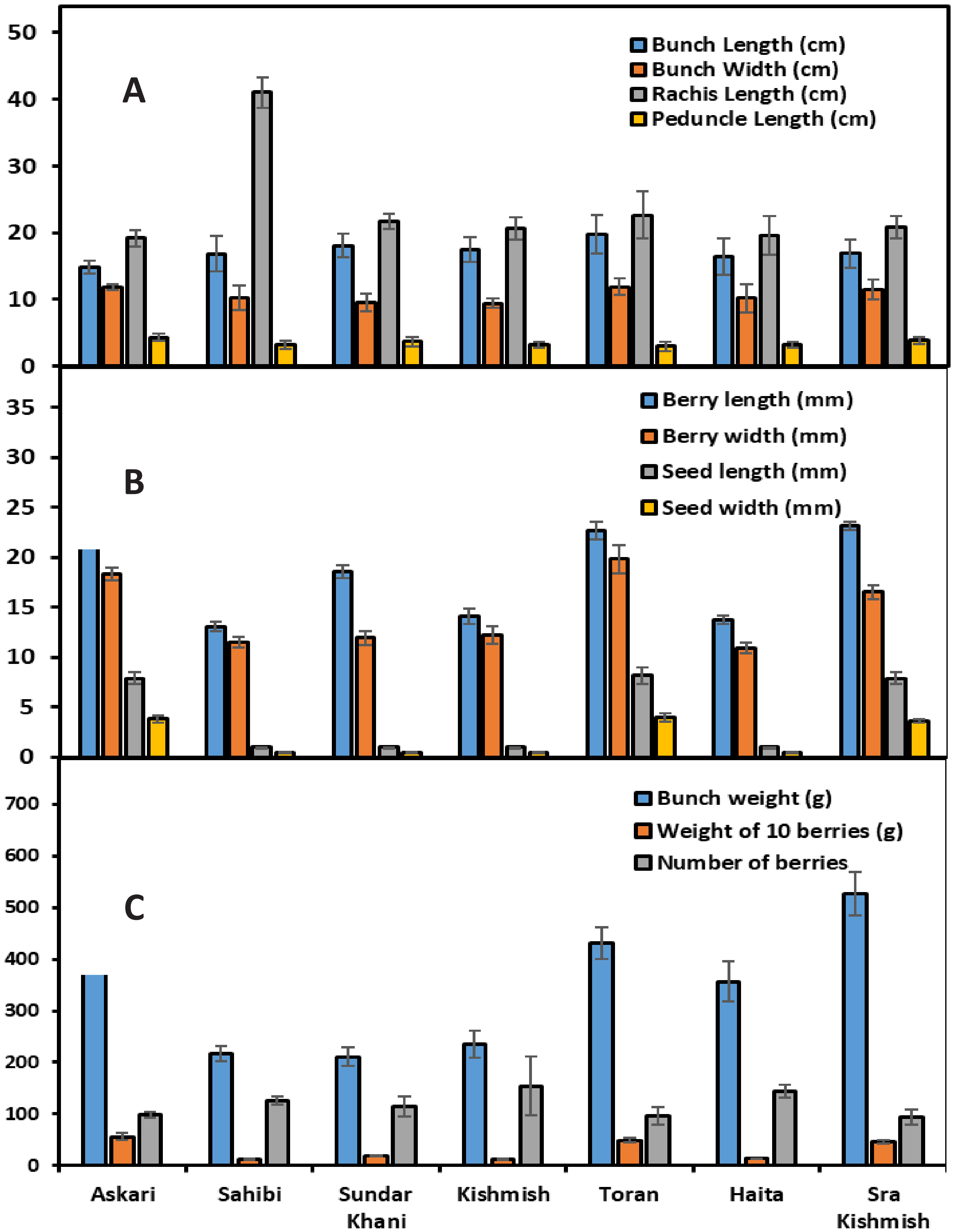

Fig. 3. Physiological traits of different grape varieties grown in Baluchistan, Pakistan

minimum berry length (23.17 mm) was recorded in 'Kishmish' (13.05 mm). The maximum berry width (19.8 mm) was observed in the 'Haita' cultivar, while the minimum berry width (10.91 mm) was recorded in the 'Sra Kishmish' cultivar. Likewise, these cultivars showed significant differences in seed length and width. The cultivar 'Haita' had the most extended seed length (8.1 mm), while 'Toran' exhibited the maximum seed width (4.01 mm), and no seed was found in 'Askari'.

Correlation of morphological traits. The results of the correlation analysis of morphological traits are shown in Table 2. The results revealed that the highest positive correlation (r = 0.99) was observed between SL and SW. Seed width also positively correlated (r = 0.986) with bunch weight and berry width (0.974). However, a negative correlation (r = –0.916) was observed between berry length and the number of berries. Likewise, a negative correlation (r = –0.868) was also observed between the number of berries and the weight of berries.

Biochemical attributes: The grape cultivars growing in Balochistan showed significant differences in biochemical attributes (Tab. 3). TSS was observed in the range between 16.26 and 24.76°Bx. The highest TSS was observed in 'Sundarkhani', while the lowest was found in 'Haita' (16.26%). Similarly, the maximum TA was observed in 'Sundarkhani' (1.58%), and the minimum was recorded in the 'Haita' cultivar (1.04%). Meanwhile, a maximum TSS: TA ratio was observed in 'Sahibi' (40.75%), and a minimum TSS: TA was exhibited in 'Haita' (21.02%). Concerning vitamin C contents, the highest contents of vitamin C (26.17 mg 100 g^{-1}) were recorded in 'Kishmish', which was on par with 'Sahibi' (25.91 mg 100 g^{-1}), whereas minimum vitamin C contents (18.13 mg 100 g^{-1}) were assessed in 'Askari'. Likewise, the pH value of grape cultivars grown in Balochistan conditions was 3.84 to 4.56.

The amount of DPPH antioxidant activity and total phenolic contents also varied significantly with grape cultivars. The highest DPPH (90.87%) was observed in 'Kishmish' at par with 'Sahibi' (90.52%) and 'Toran' (89.90%), while the minor antioxidants were noticed in 'Haita' (85.77%). Likewise, the total phenolic contents showed significant differences in grape cultivars grown in Balochistan, ranging from 113.79 to 346.50 mg GAE $L^{-1,}$ and were highest in 'Sundar Khani' (346.50 mg GAE L^{-1}), while the lowest phenol contents (113.79 mg GAE L^{-1}) were observed in 'Haita'.

Table 2. Coefficient of correlation (r) of morphological qualitative attributes of unexplored local grape cultivars growing in Balochistan, Pakistan

	BL	BW	RL	PL	bl	bw	SL	SW	BWt	Wb
BW	–0.056									
RL	0.050	–0.175								
PL	–0.687	0.345	–0.357							
Bl	0.128	0.809	–0.453	0.525						
bw	0.153	0.910	–0.313	0.301	0.889					
SL	0.011	0.953	–0.333	0.427	0.919	0.964				
SW	0.027	0.956	–0.330	0.408	0.915	0.974	0.999			
BWt	–0.173	0.889	–0.466	0.437	0.780	0.772	0.895	0.882		
Wb	–0.062	0.939	–0.370	0.523	0.930	0.962	0.983	0.986	0.856	
NB	–0.094	–0.824	0.092	–0.499	–0.916	–0.810	–0.852	–0.848	–0.674	–0.868

BL – bunch length, BW – bunch width, RL – rachis length, PL – peduncle length, BL – berry length, BW– berry width, SL – seed length, SW – seed width, WBt – weight of ten berries, WB – bunch weight, NB – number of berries

Table 3. Biochemical attributes of unexplored local grape cultivars growing in Balochistan, Pakistan

Parameters	Cultivars						
	Toran	Kishmish	Sundar Khani	Askari	Haita	Sra Kishmish	Sahibi
Total soluble solids (°Bx)	24.20 ±0.83 a	16.40 ±0.79 c	24.76 ±0.28 a	20.26 ±0.65 b	16.26 ±0.57 c	19.36 ±0.65 b	21.43 ±0.77 b
Titratable acidity (%)	1.08 ±0.47 b	1.04 ±0.20 b	1.58 ±0.07 a	1.29 ±0.16 ab	1.04 ±0.14 b	1.23 ±0.16 ab	1.35 ±0.19 ab
Vitamin C (mg 100 g^{-1})	18.37 ±1.03 bc	26.17 ±1.05a	22.72 ±1.00abc	18.13 ±1.02c	20.18 ±0.84 bc	23.32 ±0.95 ab	25.91 ±0.86 a
TSS : TA ratio	28.89 ±1.08 b	30.11 ±1.01 b	39.05 ±0.90 a	26.45 ±0.93 bc	21.02 ±1.19 c	29.10 ±1.01 b	40.75 ±1.06 a
pH	4.56 ±0.22 a	4.09 ±0.14 bc	4.22 ±0.13 b	3.85 ±0.13 d	4.11 ±0.17 b	3.94 ±0.18 cd	4.48 ±0.12 a
Antioxidant activity (%)	89.90 ±0.34 a	90.86 ±0.36 a	89.21 ±0.80 ab	87.88 ±0.52 bc	85.77 ±0.50 d	86.23 ±0.57 cd	90.52 ±0.45 a
Total phenolic (mg GAE L^{-1})	256.62 ±2.87 b	337.92 ±3.72a	346.50 ±3.21 a	152.46 ±3.17 de	113.79 ±2.86 e	232.16 ±3.19 bc	177.67 ±3.25 cd

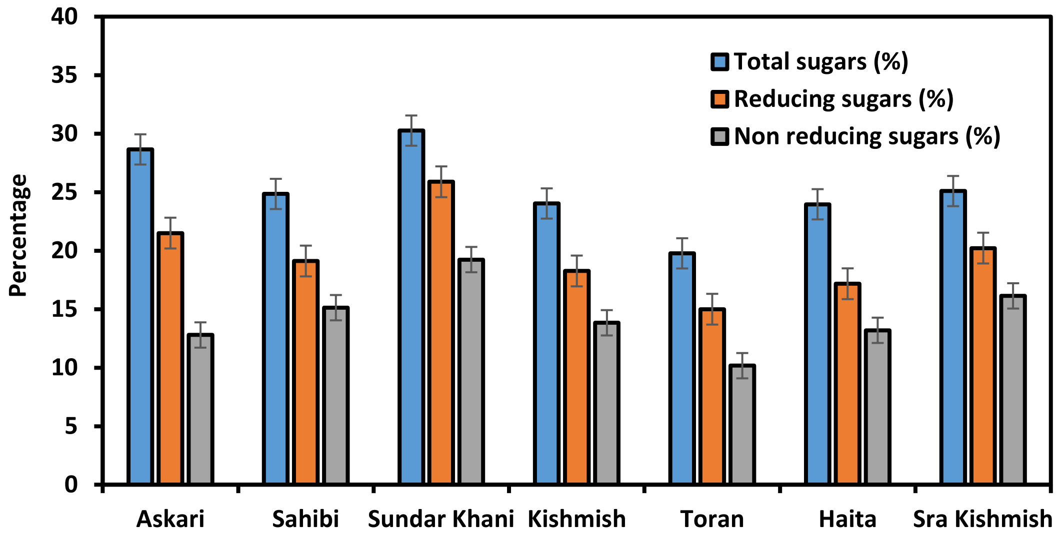

Fig. 4. Biochemical traits of different grape varieties grown in Baluchistan, Pakistan

Total sugars (%), reducing sugars (%), and nonreducing sugars (%). The data relating to total sugars, reducing sugars, and nonreducing sugars are presented in Figure 4. The results revealed a significant difference in the sugar contents of grape cultivars, and the highest total sugar content (30.26%) was observed in 'Sundar Khani', while the lowest total sugar content (19.77%) was observed in 'Toran'. However, the highest reducing sugars were noticed in 'Sundar Khani' (21.88%), followed by 'Askari' (19.80%), while the highest nonreducing sugar contents were highest in 'Haita' (8.79%) and lowest in 'Askaris' (8.40%).

Mineral contents: The grape cultivars grown in Baluchistan showed significant differences in their mineral contents. The available contents of N, P, and K are shown in Figure 5. The results revealed that N was in the range from 0.08 to 0.16%, and it was highest (0.16%) in 'Askari' and 'Sahibi', while it was observed least in 'Sra Kismish' (0.08%). Likewise, the K contents in these genotypes were also variable and were recorded at a maximum (0.52%) in 'Sahibi' and a minimum in 'Toran' (0.24%). However, P was highest in 'Sundar Khani' (0.47%) and lowest (0.16%) in 'Askari'. The data regarding Na and Ca are shown in Table 4, and Na was noted as a maximum (7.46 mg L^{-1}) in 'Sahibi' and a minimum (6.46 mg L^{-1}) in 'Toran'. However, the Ca (427.67 mg L^{-1}) content was highest in a similar cultivar and was lowest (229 mg L^{-1}) in 'Sundar Khani'.

Regarding micronutrients, the concentrations of observed micronutrients were highly variable in the studied grape cultivars (Tab. 4). Among these cultivars,

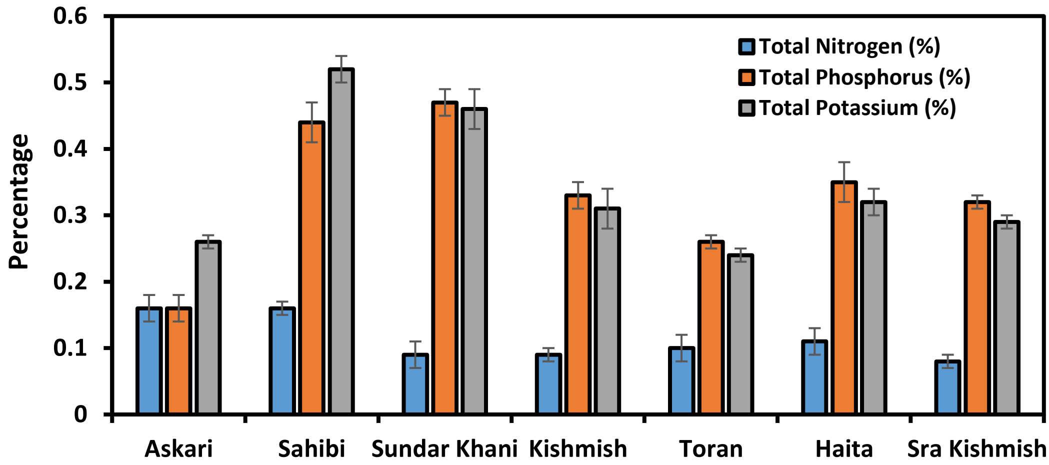

Fig. 5. Availability of N, P, and K minerals in local grape cultivars grown in Baluchistan, Pakistan

Table 4. Content of macro- and micronutrients (mg L^{-1}) in grapes local cultivars growing in Balochistan, Pakistan

Nutrient	Cultivars						
	Askari	Sahibi	Sundar Khani	Kishmish	Toran	Haita	Sra Kishmish
Sodium	6.83 ±0.26 ab	7.46 ±0.39 a	7.13 ±0.36 ab	7.33 ±0.37 a	6.56 ±0.36 b	6.76 ±0.48 ab	7.13 ±0.28 ab
Calcium	357.67 ±1.79 c	343.67 ±2.12 c	229.00 ±1.93e	406.67 ±1.64 b	427.67 ±2.16 a	318.33 ±1.64 d	408.67 ±1.87 ab
Zinc	4.45 ±0.55 ab	2.58 ±0.28 d	3.46 ±0.27 c	3.93 ±0.15 bc	3.31 ±0.45 cd	4.01 ±0.12 bc	5.18 ±0.28 a
Iron	86.33 ±1.85b	65.33 ±1.9c	110.33 ±1.23a	70.66 ±1.47c	67.66 ±1.88c	45.00 ±1.63d	65.66 ±1.77c
Copper	4.70 ±0.29 b	3.13 ±0.26 c	3.13 ±0.35 c	2.63 ±0.34c	4.93 ±0.28 b	5.96 ±0.14 a	4.36 ±0.46 b
Cobalt	0.60 ±0.17 bc	0.75 ±0.1 5b	0.46 ±0.18 c	0.33 ±0.10 c	1.19 ±0.21 a	1.36 ±0.32 a	0.82 ±0.25 b
Manganese	0.72 ±0.28 ab	0.66 ±0.15 a–c	0.45 ±0.15 cd	0.49 ±0.13 b–d	0.76 ±0.20 a	0.32 ±0.13 d	0.80 ±0.29 a

Table 5. Coefficient of correlation (r) of biochemical attributes of unexplored local grape cultivars growing in Balochistan, Pakistan

	TS	RS	NRS	TSS	TA	Vit C	TSS:TA	pH	AA	TPC	Ca	Fe	Zn	Mn	Co	Cu	N
RS	0.991																
NRS	0.497	0.383															
TSS	0.128	0.213	–0.531														
TA	0.832	0.875	0.065	0.575													
Vit C	0.027	0.046	–0.167	–0.171	0.196												
TSS:TA	–0.036	–0.024	–0.162	–0.021	0.154	0.396											
pH	–0.027	0.021	–0.315	–0.163	0.013	0.164	0.735										
AA	–0.018	0.042	–0.345	0.166	–0.056	–0.166	–0.789	–0.29									
TPC	0.114	0.167	–0.26	0.401	0.242	0.085	–0.756	–0.585	0.832								
Ca	–0.298	–0.215	–0.631	0.065	–0.287	–0.162	–0.386	0.226	0.82	0.437							
Fe	0.146	0.137	–0.052	0.294	0.339	0.32	0.515	–0.044	–0.554	–0.312	–0.531						
Zn	–0.1	–0.119	0.061	–0.663	–0.421	–0.028	0.353	0.68	–0.146	–0.624	0.278	–0.081					
Mn	0.082	0.183	–0.651	0.561	0.258	–0.321	0.084	0.436	0.366	0.091	0.623	0.049	0.199				
Co	–0.402	–0.418	0.066	–0.051	–0.475	–0.723	–0.274	–0.014	0.091	–0.1	0.176	–0.688	–0.033	–0.027			
Cu	–0.309	–0.36	0.286	–0.323	–0.598	–0.829	–0.236	0.037	–0.015	–0.363	0.131	–0.515	0.34	–0.006	0.859		
N	0.784	0.773	0.426	0.352	0.624	–0.422	–0.518	–0.474	0.3	0.405	–0.119	0.024	–0.364	0.172	–0.094	–0.018	
P	0.129	0.132	0.07	0.194	0.423	0.557	0.42	0.017	–0.476	–0.012	–0.595	0.162	–0.533	–0.464	–0.14	–0.491	–0.19

TS – total sugars, RS – reducing sugars, NRS – non reducing sugars, TSS – total soluble solids, TA – titratable acidity, Vit C – vitamin C, AA – antioxidant activity, TPC – total phenolic content, Ca – calcium, Fe – iron, Zn – zinc, Mn – manganese, Co – cobalt, Cu – copper, N – nitrogen, P – phosphorus

'Sra Kishmish' was enriched with Zn and had a maximum (5.18 mg L^{-1}) Zn, while it was observed lowest (2.58 mg L^{-1}) in the 'Sahibi' cultivar. However, Fe was highest (110.33 mg L^{-1}) in 'Sundar Khani' and was minimal (45 mg L^{-1}) in 'Haita', while it had the highest amounts of Cu (5.96 mg L^{-1}) and Co (1.36 mg L^{-1}). Similarly, Mn contents were found at a maximum (0.79 mg L^{-1}) in 'Sra Kishmish' and a minimum (0.32 mg L^{-1}) in 'Haita'.

Correlation analysis of biochemical traits. The results regarding the correlation analysis of grapes are shown in Table 5. The results showed a strong correlation (r = 0.991) between total and reducing sugars. Similarly, cobalt and copper also showed a significant positive correlation (r = 0.859). The studies also showed a significant positive correlation (r = 0.832) between total phenolic contents and antioxidant activities. A negative correlation (r = 0.832) was observed between copper and vitamin C.

DISCUSSION

Morphological characterization. Information regarding fruit traits is highly valuable, as it provides insight for breeders to improve genotype and variety development. Moreover, these physical bunch traits and berry traits, such as bunch length, width, weight, berry color, and shape, are quality traits that attract consumers. These quality traits are highly affected by environmental conditions and cultivar genetic makeup. In this study, the grapes grown in Balochistan exhibited significant variations in bunch and berry traits, as 'Haita' had the maximum bunch length and 'Askari' had the maximum berries in the bunch. In grapes, these traits significantly enhance grape production and are also preferred by consumers. Similar findings were observed by Unal et al. [2014], who stated that the trait number of berries is crucial in evaluating grape quality, especially in table grapes. These results were in line with the findings of many researchers [Fahmi et al. 2012, Uddin et al. 2011]. Akram et al. [2020] also found maximum bunch length in local cultivars compared to exotic cultivars. Similar facts were noted by other researchers who demonstrated that bunch length varies with cultivar, depending on genetic and climatic conditions [Davies and Savolainen 2006, Sabry et al. 2009, Wahab 2011]. Berry traits such as berry size and weight are correlated and influenced by physiological activities such as cell growth and division and are highly influenced by environmental conditions and cultural practices. Variations in climatic conditions and cultural practices affect berry size and chemical composition [Rolle et al. 2015]. However, an extensive berry size results in fewer berries in a bunch [Joshi et al. 2015].

Biochemical characterization. Determining grapes' biochemical attributes is essential for breeders and the viticulture industry to classify them in flavor and quality. In grapes, flavor is a complex trait; a blend of sugars and acids determines its quality. Moreover, the presence of sugars and acids affects its taste, quality, and market value [Shiraishi et al. 2010]. TSS and titratable acidity significantly improve fruit quality attributes in grapes and play an intermediate role in physiological processes such as berry ripening and softening [Campbell et al. 2021]. In our findings, TSS was observed in the range 16.26 to 24.76°Bx and is considered a maturity parameter for grape harvesting. TSS is associated with tissue breakdown to a greater extent, which leads to the release of sugars, while the pectinase enzyme converts insoluble pectin into soluble solids [Arsad et al. 2015, Hmid et al. 2016]. Similar values were observed by Fahmi et al. [2012], who characterized different grape genotypes and found TSS in the range of 12–25°Bx. Likewise, Aponso et al. [2017] confirmed that the TSS of most genotypes is up to 19.83%.

Titratable acidity is another critical attribute that substantially impacts sensory quality, and an increase in TA produces acidity in berries. Highly acidic genotypes are used in the wine industry, while low acidic genotypes are consumed for fresh consumption. In our findings, TA was observed in the 1.04 to 1.58% range as these cultivars were consumed as table grapes. These results agreed with Akram et al. [2020], who found TA in the range from 0.43–1.36% in European grapes and found that environmental and genetic factors variate its composition. Moreover, the TSS : TA ratio determines grape maturity [Zoecklein 2001, Campbell et al. 2021]. The TSS:TA ratio represents the balance between sugar and acid, is considered significant for assessing overall fruit quality, and is a widely accepted biochemical index for evaluating table grape quality [Mota et al. 2006, Champa 2015].

In this study, the TSS : TA ratio in grape cultivars grown in Balochistan ranged from 21.02 to 40.75%, which is acceptable for good-quality table grapes. Crisosto and Smilanick [2002] claimed that grapes should be harvested when the TSS : TA ratio is approximately 20%. However, due to certain factors, such as environmental conditions, storage period, and genotypes, the TSS:TA ratio may vary [Liu et al. 2006]. The pH of the grape cultivars studied was between 3.85 and 4.56, consistent with the findings of Soltekin et al. [2015], who determined the pH values of grapes in a similar range.

Vitamin C is another essential constituent that develops a better human immune system and prevents certain skin diseases. The grape cultivars grown in Balochistan were rich in vitamin C, phenolics, and antioxidants. However, the amount of the constituents varied with the cultivars. Phenolic compounds and antioxidants are highly beneficial for human health and essential to the human diet, as they are anticancer agents and prevent certain cardiovascular diseases [Rana and Bhushan 2016]. Worldwide, there is an ever-increasing demand for antioxidants, and using grapes in the daily diet may reduce their synthetic uptake [Garrido et al. 2011]. Similarly, huge variations were observed in sugar contents and varied from cultivar to cultivar. It might be due to genetics, soil, climate, or cultivation practices [Liu et al. 2006, Yinshan et al. 2017]. Our results were in line with the findings of other researchers who found sugar variations while studying different grape cultivars [Munoz-Robredo et al. 2011, Akram et al. 2020].

Mineral characterization. Minerals are essential inorganic substances required by humans to perform their physiological functions and are classified into macro- and microelements. Typically, macrominerals are required at 100 mg dl^{-1}, while microelements are required at less than 100 mg dl^{-1} [Murray et al. 2000]. Each element has a specific role in the human body, as N is the building block of proteins, and K acts as an electrolyte and is necessary to maintain the functioning of vital organs such as the heart, muscles, brain, and kidney tissues [Siahnouri et al. 2013]. Phosphorus is the main component of deoxyribonucleic acid and adenosine triphosphate and is needed to produce energy, protein, and DNA synthesis. However, these minerals are an integral part of plants' structure, are involved in specific plant metabolisms, respond as enzyme activators, and maintain osmotic balance [Soetan et al. 2010]. In grapes, potassium is essential in berry development and is responsible for maintaining fruit and wine quality [Martins et al. 2012]. Manganese is essential for sugar metabolism-regulating enzymes, which are also used to process energy, membrane permeability, and muscle and nerve conduction [Gorgulu et al. 2016].

Grapes are enriched with minerals, provide optimum pH for blood circulation, and promote tooth and bone growth [Keskin et al. 2019]. The grape cultivars grown in Balochistan were enriched with minerals and showed a significant difference in macro- and micromineral concentrations depending upon the cultivar. In our findings, macroelements such as (N, 0.08 to 0.16%), (P, 0.16–0.47%), and (K, 0.24–0.52%) were observed in the following ranges. Ca was maximum (427.67 mg L^{-1}) in 'Sahibi', and its minimum value (229 mg L^{-1}) was noted in 'Sundar Khani'. Similar findings were observed by other researchers for nitrogen [Sensoy 2015], phosphorous [Harmankaya et al. 2012, Miele et al. 2015], potassium [Gurak et al. 2010], and calcium [Rizzon and Link 2006, Gurak et al. 2010].

Similarly, micronutrients have a significant role in human metabolism; for example, Fe is essential in living beings because it synthesizes DNA, transports oxygen, and participates in other metabolic functions. Moreover, it mediates enzymatic activities and is recommended to treat anemia [Arslan et al. 2005]. Similarly, zinc is a vital component of many enzymes involved in many physiological processes, such as energy metabolism and protein synthesis [Ma and Betts 2000]. The grape cultivars were enriched with the micronutrients Fe (45–110.33 mg L^{-1}) and Zn (2.58–5.18 mg L^{-1}), observed in the following ranges. This considerable variation may be due to environmental, soil, fertilization, and climatic conditions. Our findings agreed with Jalbani et al. [2010], who described the iron content as 50–100 mg L^{-1} in different grape cultivars. Likewise, [Sani 2013] observed variations in grape genotypes due to processing conditions and environmental factors. Similarly, the Zn concentrations observed in our study resembled and were in the range of other researchers [Onianwa et al. 2001, Dani et al. 2012, Demir et al. 2020].

CONCLUSIONS

The unexplored local grape genotypes grown in Balochistan showed significant variations based on physicochemical and mineral contents. In physical evaluation, these cultivars were well adapted to the Balochistan climate and were found to have high yield and quality traits. In biochemical traits, TSS was observed in the range of 16.26 to 24.76°Bx, while TA was observed from 1.04 to 1.58%. These cultivars were enriched with phenolic and antioxidant compounds that prevent humans from certain chronic diseases, and the values of these compounds were noted in the following ranges: 113.79–346.50 mg GAE L^{-1} and 85.77 – 90.87%, respectively. Similarly, macro- and microelements in these cultivars were high; however, their contents varied with cultivars, such as N (0.16%) and K (0.52%), which were highest in 'Sahibi'. Overall, 'Toran' performed significantly better than the other cultivars growing in Balochistan. Additionally, it was enhanced with calcium, total soluble solids, and antioxidants. The study can also provide insight for breeders to improve cultivars and value addition.

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