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Effect of Oxalic Acid on Fruit Quality and Storage Life of Blackberry (Rubus spp)

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Abstract

Blackberries hold a significant economic importance, renowned for its high nutritional content. Blackberries have shorter shelf life due to high metabolic activity, typically ranging from 2 days at 0°C. Therefore, the present study was done to investigate the effect of oxalic acid on fruit quality and shelf life of blackberries (Rubus spp.). This study was divided into two experiments. In experiment 1, two cultivars of blackberries (thorny and thornless) were harvested to screen out the best performing cultivar. In experiment 2, different oxalic acid treatments (T0: control, T1: 1.5 mM oxalic acid, T2: 2.5 mM oxalic acid and T3: 3.5 mM) were applied on best performing cultivars to extend the shelf life during storage period (3 to 12 days). After harvesting, fruit was brought to the postharvest and central lab of PMAS-Arid Agriculture University Rawalpindi for physicochemical analysis. Results revealed that thorny cultivar exhibited significant variations in terms of Physical (Fruit size, Firmness), Biochemical (TSS, TA, juice pH, total sugars) and proximate (crude fiber, total carbohydrate, moisture and fat) parameters. Moreover, experiment 2 results revealed that among different oxalic acid treatments, T1 (1.5mM) performed best for maintaining shelf life and quality of blackberry fruit.

Key words: Black Berries; Fruit quality; Oxalic Acid; Shelf Life

Introduction

Blackberry (Rubus L.) is a prominent fruit due to its distinct color, flavor, and taste. Over the last few decades, the consumption of fresh blackberries has increased due to high contents of minerals, vitamins, phenolic compounds, and dietary fibers. Based on biological analysis, it has been proven that blackberries are effective against chronic diseases in humans due to its medicinal and nutraceutical properties [Sabir et al., 2019: Seeram, 2013]. Blackberries has also the ability to decrease brain ageing in rats [1]. Blackberries are highly perishable because they have fragile thin skin and high respiration rate. Change in physicochemical properties and fast ripening in blackberries are due to soft tissue, delicate skin and higher respiration rate that hamper postharvest storage and marketing [2] (Han et al. 2004). Moreover, blackberries' postharvest life is also hampered by their susceptibility to physical injuries, softening, water loss and postharvest diseases such as Rhizopus rot and grey mold [3]. That's why blackberry fruits are unmarketable after 2 to 3 days at 0°C due to leakage and fruit rot (Sabir et al., 2019). Conventionally grown black berry fruits can maintain marketable quality for maximum 7 days when stored at 2±0.5 ºC with 90-95% relative humidity [3].

Due to limited growing season and shorter shelf life, blackberries are subjected to various processing techniques including freezing, canning, drying, jams, and jellies [4,5]. The freezing process has been identified as the processing method that causes the least amount of damage to the phenolic compounds present in blackberry fruit [6]. Commercial cultivation of blackberries in Pakistan is limited due to poor shelf life. In Pakistan only two research institutes namely Barani Agriculture Research Institute Chakwal and Ayub Agriculture Research Centre Tarnab are producing two varieties of blackberries (thorny and thornless varieties). Researchers are struggling to extend the shelf life and preservation of fruits and vegetables from farm to fork. Globally, different findings have been reported by researchers for maintaining quality, shelf life and storage of horticultural produces during supply chain. Significant results have been shown in extending storage life and maintaining quality during postharvest period with respect to cold storage, modified atmosphere packaging, controlled atmospheres, hypobaric storage, ozonation, and pre-storage heat treatments (Hasan et al., 2020; Maryam et al., 2021; Singh, 2022; Zhang and Jiang, 2019).

Due to restriction on the use of these technologies, several chemical compounds for safe consumption have been evaluated for maintain quality during storage. Thes include 1-methylcyclopropene (1-MCP) (Dias et al., 2021), nitric oxide and organic edible coatings (Hasan et al., 2021). Exogenous treatment of various organic acids is important for maintaining the control of ripening and senescence during postharvest storage and enhancing resistance against biotic and abiotic stresses (Walker and Famiani, 2018). In higher plants oxalic organic acid is naturally occurring that plays an essential role in several metabolic processes during growth and development. It has been observed that before and after harvest application of oxalic acid is beneficial for enhancing physical, biochemical quality of fruit at harvest. Oxalic acid application also maintains antioxidant capacity, regulates metabolic processes and lower storage rot and diseases. Postharvest application of oxalic acid on fruits and vegetables also delayed ripening and senescence, mitigate enzymatic browning and prevention of chilling injury (Hasan et al., 2023). Application of 2mM oxalic acid on Blueberry showed significant increases in firmness, total anthocyanins, and antioxidant capacity (Retamal-Salgado et al., 2023). In addition, (Razzaq et al., 2015) have reported that dip treatment of 5 mM oxalic acid on 'Samar Bahisht Chaunsa' showed effectively delayed in ripening and senescence by limiting ethylene production and softening of enzyme activity during ripening and storage.

Similarly, 1mM (preharvest) oxalic acid application on 'Samar Bahisht Chaunsa' mangoes minimize water loss (Razzaq et al., 2015). (Aslam et al., 2020) have reported that application of 2 mM oxalic acid on jamun fruit increased vitamin C contents. Moreover, 1% oxalic acid increased the activity of peroxidase enzyme (Shafique et al., 2023). Preharvest application of 2 mM oxalic acid increased the fruit size, delayed ripening, and retained higher antioxidants in apricot fruit at ambient conditions (Ahmed et al., 2021). To extend the shelf life and storage period of black berries there is a dire need to develop strategies for maintaining quality and marketability. From above facts it has been noticed that previously no or limited work has been done on postharvest application of oxalic acid on blackberries to maintain quality and shelf life. Therefore, the present study was conducted to evaluate the effect of oxalic acid on fruit quality and storage life of blackberries (Rubus spp.) fruit.

Materials and Method

The study was conducted in the post-harvest and central research laboratory of PMAS-Arid Agriculture University Rawalpindi. Two experiments were conducted for this study to evaluate the effect of cultivars and oxalic acid on fruit quality and shelf life of blackberries

Experiment 1:

Two cultivars of blackberries (thorny and thornless) were harvested from two different farms to evaluate the effect of cultivars on fruit quality of blackberries. Thorny variety was harvested from Ijaz khan Farm located in Madrota Attock, while thornless variety was obtained from Agricultural and Research Centre Peshawar. Fruits were brought to post-harvest and central research laboratory of PMAS-Arid Agriculture University Rawalpindi for physicochemical analysis.

Physical quality parameters

Among physical parameters, fruit shape and length of blackberries varieties were determined by using digital vernier caliper and expressed in millimeter (mm) (Abbasi et al., 2016). The calculation of Geometric Mean Diameter was performed Based on the formula as outlined by (Abbasi et al., 2016).

$$Dg = (LWT)\ 0.333$$

The calculation of surface area (S) in millimeters squared was noted by using formula as outlined by [7].

$$S = \pi\ Dg2$$

Where Dg is the geometric mean diameter of the Blackberry.

The sphericity of fruit samples was determined by using formula as outlined by (Ahmadi et al., 2008)

$$\Phi = (Dg/\ L) \times 100$$

Skin color of blackberries fruit was checked by using chromameter (CR-400, Konica Minolta Sensing, Inc., Japan). The evaluation of skin color was done using fruits that were kept separately. The parameters used to assess fruit skin color are L*, a*, and b*. L* values indicate the level of lightness, with higher positive values indicating greater lightness and negative values indicating darkness. Negative a* numbers mean a greenish hue, while positive numbers suggest redness. Similarly, negative b* numbers suggest blueness, while greater positive numbers suggest yellowness. The weight loss was determined by the method mentioned by [8].

Biochemical quality parameters

Total soluble solids were measured by using digital refractometer (Atago-PAL-1, Tokyo, Japan) and expressed as ºBrix (Sinha & Sinha, 2017). The pH of samples was recorded by using a digital pH meter (HI2211 HANNA-USA) and the testing was performed using standardized buffering agents, following the prescribed calibration technique (Shetgar et al., 2018). Titratable acidity as malic acid by using 0.1N NaOH was assessed by method described by Association of Official Analytical Chemists in their 2005 publication, specifically method number 942.15. Total sugars and reducing sugar were also determined by using AOAC method no. 968.28 (Abbasi et al., 2016).

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Proximate composition

The moisture contents were calculated by AOAC method no 930.15 in drying oven until a uniform weight was achieved. Additionally, a calculation of crude fat was performed. The measurements were noted the

ST 243 Soxtec extraction of solvent system in accordance with the (AOAC, 2005) method no. 930.09. The measurement of crude protein was conducted using the (AOAC, 2005) method no. 977.02, utilizing the FOSS Kjeltec 8400 Analyzer Unit [9]. In a similar manner, the analysis of crude fiber and ash content was recorded by using the methods outlined in AOAC (2005) (Abbasi et al., 2016).

Nutraceutical attributes

Ascorbic acid contents in the pulp of blackberry fruits were determined by using the technique described by (Hans, 1992). Total phenolic contents were recorded using the FC reagent [10]. Similarly, total flavonoid compounds (TFC) were measured by using a method outlined by [10].

Experiment 2:

Based on the findings of previous experiment, thorn cultivar was found to be best for physicochemical analysis. Therefore, this experiment was designed to check the impact of oxalic acid on best performing

cultivar from experiment 1 for quality analysis. Four treatments were used in this experiment and each

treatment containing 40 fruits. Treatments include T0: control, T1: 1.5 mM oxalic acid, T2: 2.5 mM oxalic acid and T3: 3.5 mM oxalic acid. In each treatment fruits were dipped in oxalic acid for 3 minutes. After treatments fruits were kept at 6°C in cold stored for further analysis with three days interval. Parameters including total soluble solids (TSS), pH, color, titratable acidity, total Sugars, reducing Sugars, ascorbic acid, Total Phenolic Content and Total Flavonoid Content was taken as mentioned in experiment 1.

Statistical Analysis:

In experiment 1, T-Test was done to evaluate suitable variety by using SPSS software. In experiment 2, storage study was done by using annova technique under Completely Randomized Design (CRD). Statistical analysis was done by using statistics 8.1.

Results and Discussion

Physical Parameters:

Results regarding physical parameters are presented in table 1. Results showed significant variations between two blackberry cultivars. Results indicated that higher fruit size (76.27 mm), GMD (25.2 mm3), surface area (200.35 mm2) and fruit firmness (1005.66 gm) were recorded in thorny cultivar as compared to thornless. However, sphericity (85.34%) was recorded in thornless cultivar. The assessment of physico- chemical properties holds significant importance in determining the acceptance of consumers and has also been demonstrated to be effective in distinguishing between different cultivars [11]. The visual characteristics of berries contribute to the determination of berries required for potential value-added processes [12]. Generally, fruit size is an appearance characteristic that will be of primary concern in the fresh fruit consumer market. However, for soft and juicy blackberry fruits, hardness is also an important index because blackberries are aggregate berries that lack a complete protective cuticle (Garcia Munoz et al., 2020) (Table 1).

Table 1: Physical Parameters of Blackberry Cultivars.

Cultivars	Fruit Size mm	GMD mm^3	Sphericity %	Surface Area mm^2	Fruit Firmness (gm)
Thorny	76.27±0.63	25.02±0.11	78.67±0.65	200.35±0.33	1005.66±0.88
Thornless	33.33±0.70	17.8±0.49	85.34±0.36	100.37±0.33	991.00±0.57

Results are the average of three replication with a ± standards errors.

Biochemical Parameters

Results revealed significant variations in both cultivars of blackberry for biochemical parameters. Significantly higher TSS (10.15ºBrix), juice pH (3.20), TA (1.3%), Total sugars (10.02%), and reducing sugars (9.50%) were noted in thorny cultivar as compared to lower TSS (6.53 ºBrix), juice pH (3.0), TA (1.1%), Total sugars (8.93%), and reducing sugars (8.12%) in thornless cultivars as presented in Table 2. Similarly, variations among total soluble solids among different cultivars as early reported by (Miletić et al, 2006) and [13]. The findings of (Basaran & Kepenek, 2011) as well as [14] align with our results, indicating that the pH average for 'Chester Thornless' and 'Navaho' were 2.91 and 2.9 units. Previous studies in literature have documented variations among cultivars with respect to titratable acidity (TA) [15] (Miletić et al., 2006; Basaran & Kepenek, 2011). In contrast, the cultivars 'Black Satin' and 'Thornless' exhibited the minimum rates of Reducing Sugar and Total Sugar [16].

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Table 2: Biochemical parameters of Blackberry cultivars.

Cultivars	TSSºBrix	pH	TA (%)	Total Sugars %	Reducing Sugars%
Thorny	10.15±0.43	3.20±0.05	1.3±0.05	10.02±0.12	9.50±0.27
Thornless	6.53±0.60	3.00±0.05	1.1±0.11	8.93±0.10	8.12±0.26

Results are the average of three replication with a ± standards errors.

Table 3: Nutraceutical parameters of Blackberry cultivars.

Cultivars	Ascorbic acid (mg 100 g -1 FW)	Total phenolic content (mg GAE g -1 DE)	Total flavonoid content (mg RU g -1 DE)
Thorny	43.03±0.19	67.44±0.66	10.16±0.38
Thornless	37.47±0.71	61.81±0.58	7.24±0.32

Results are the average of three replication with a ± standards errors.

Table 4: Nutritional parameters of blackberry cultivars in 100g.

Cultivars	Moisture Content %	Crude Fiber%	Crude Protein%	Ash Content%	Total Carbohydrate%	fat %
Thorny	79.47±0.64	7.91±0.48	2.81±0.41	0.82±0.00	9.74±0.54	0.65±0.00
Thornless	72.54±0.93	5.74±0.32	1.87±0.37	0.43±0.01	9.68±0.34	0.47±0.03

The results are the average of three replications, with a ± standard error.

Table 5: pH and Tss of Blackberry.

	pH				TSS (Brix)			
Treatments	3 Days	6 Days	9 Days	12 Days	3 Days	6 Days	9 Days	12 Days
T0	2.6±0.06	2.7±0.06	3.6±0.10	4.5±0.08	9.4±0.08	8.4±0.06	7.6±0.04	7.2±0.06
T1	2.2±0.08	1.8±0.10	2.4±0.12	3.6±0.12	8.8±0.24	9.1±0.20	7.6±0.16	9±0.24
T2	0.82±0.01	1.1±0.16	1.5±0.14	2.8±0.12	8.7±0.26	9.2±0.13	7.7±0.16	9.4±0.18
T3	0.89±0.01	0.9±0.12	1.4±0.14	2.8±0.12	8.2±0.10	9.4±0.22	8.4±0.12	10.5±0.44

The results are the average of three replications, with a ± standard error.

Table 6: Weight loss and Ascorbic acid of blackberry.

	Weight loss (%)				Ascorbic Acid (%)			
Treatments	3 Days	6 Days	9 Days	12 Days	3 Days	6 Days	9 Days	12 Days
T0	7.8±0.16	14.8±0.10	32.1±0.16	44.3±0.12	41.3±0.31	36.8±0.14	30.7±0.22	24.4±0.38
T1	7.6±0.12	13.4±0.33	15.7±0.20	17.9±0.20	42.0±0.16	37.4±0.31	33.2±1.24	29.5±1.67
T2	5.7±0.14	10.5±1.24	16.36±0.30	18.4±0.33	44.4±0.91	39.6±1.13	34.1±1.65	30.4±2.0
T3	6.5±0.28	16.3±1.14	17.6±0.71	26.5±1.53	43.9±0.95	38.9±1.3	34.9±1.2	29.8±2.1

The results are the average of three replications, with a ± standard error.

Table 7: Firmness and TA of Blackberry cultivar.

	Firmness (gm)				TA (%)			
Treatments	3 Days	6 Days	9 Days	12 Days	3 Days	6 Days	9 Days	12 Days
T0	241±0.23	1006±0.40	987±0.40	265±0.40	0.85±0.04	0.79±0.01	0.66±0.04	0.58±0.02
T1	398±0.81	1031±0.62	255±1.02	903±0.81	0.71±0.01	0.67±0.04	0.63±0.03	0.51±0.02
T2	662±0.84	975±1.22	785±1.02	325±0.40	0.69±0.04	0.58±0.08	0.53±0.02	0.48±0.03
T3	805±1.08	515±0.81	927±1.64	436±1.24	0.64±0.01	0.60±0.08	0.52±0.02	0.48±0.03

The results are the average of three replications, with a ± standard error.

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Table 8: Reducing Sugar and Total Sugar of blackberry.

	Reducing Sugars (%)				Total sugar (%)			
Treatments	3 Days	6 Days	9 Days	12 Days	3 Days	6 Days	9 Days	12 Days
T0	5.6±0.31	6.03±0.02	8.3±0.40	8.72±0.20	12.4±0.36	13.7±0.06	13.9±0.18	14±0.81
T1	6.03±0.01	8.22±0.24	9.05±0.01	9.45±0.02	11.23±0.77	12.46±0.37	13.65±0.19	16.1±1.65
T2	5.55±0.38	8.25±0.24	8.93±0.09	9.30±0.10	14.3±0.37	14.7±0.44	15.5±0.79	15.4±2.0
T3	5.58±0.38	7.35±0.19	8.33±0.27	8.84±0.02	14.5±0.39	15.0±0.47	15.5±0.79	15.4±2.0

The results are the average of three replications, with a ± standard error.

Table 9: Total Phenolic Content and Total Flavonoid Content.

	Total Phenolics				Total Flavonoid (%)			
Treatments	3 Days	6 Days	9 Days	12 Days	3 Days	6 Days	9 Days	12 Days
T0	64.41±0.90	59.45±0.31	47.44±0.44	43.47±0.46	10.24±0.72	9.67±1.14	8.36±0.84	9.35±0.77
T1	65.22±1.09	66.30±3.17	62.51±2.80	60.37±0.77	18.25±0.91	16.61±0.91	17.29±0.83	22.21±0.77
T2	61.38±0.31	63.61±2.02	58.62±4.20	54.49±3.22	13.13±1.20	14.38±1.72	14.40±0.39	17.35±1.18
T3	68.48±2.54	69.75±1.62	61.45±3.18	57.49±2.00	16.36±0.17	18.60±0.73	19.47±1.66	20.35±0.13

The results are the average of three replications, with a ± standard error.

Table 10: Color parameters of *L** and *a** of blackberry

	*L**				*a**			
Treatments	3 Days	6 Days	9 Days	12 Days	3 Days	6 Days	9 Days	12 Days
T0	54.04±0.82	52.46±1.55	32.92±0.64	19.52±3.31	9.19±0.50	13.32±0.79	18.61±0.84	24.59±1.65
T1	51.27±2.04	47.03±2.11	39.42±1.66	24.64±1.29	9.22±0.505	14.27±0.39	17.41±1.24	20.43±3.28
T2	55.36±1.17	46.39±2.51	34.46±0.37	21.31±1.68	8.84±0.26	12.68±1.00	17.45±1.24	19.32±1.65
T3	50.36±0.87	43.54±2.10	33.49±0.77	20.51±1.28	8.79±0.12	13.14±1.01	17.46±1.24	19.41±1.65

The results are the average of three replications, with a ± standard error.

Table 11: Color *b** parameter of blackberry.

	*b**			
Treatments	3 Days	6 Days	9 Days	12 Days
T0	24.41±1.58	28.39±1.61	32.38±1.61	37.40±2.02
T1	25.37±1.17	30.57±0.80	31.40±1.20	35.48±1.20
T2	23.30±1.98	27.26±2.02	30.60±0.80	31.34±0.43
T3	22.97±1.98	26.94±2.04	30.37±0.79	31.67±0.47

The results are the average of three replications, with a ± standard error.

Nutraceutical Parameters

Results for nutraceutical parameters were found to be significant for both blackberry cultivars. Significantly maximum ascorbic acid (43.03 mg 100 g -1 FW), total phenolic (67.44 mg GAE g-1 DE) and total flavonoid contents (10.16 mg RU g -1 DE) in thorny cultivar as compared to minimum ascorbic acid (37.47 mg 100 g -1 FW), total phenolic (61.81 mg GAE g-1 DE) and total flavonoid contents (7.24 mg RU g -1 DE) as shown in table 3. Similarly, variations among blackberry cultivars were also noted for ascorbic acid ranging from 25.6 mg g-1 to 69.2 mg g-1 (Basaran & Kepenek, 2011). Moreover, thorny plants had greater quantity of total phenolics as compared to thornless plants (Clark et al., 2002: Cho et al., 2005). Previous studies have documented a high degree of variations among different blackberry varieties (Siriwoharn et al., 2004). The variations may be attributed to environmental factors, planting conditions, and harvest maturity (Cho et al., 2005) (Table 3).

3Proximate composition

Statistically significant results were obtained for both cultivars as depicted in (Table 4). Higher moisture content (79.47%), Crude fiber (7.91%), Crude protein (2.81%), Ash content (0.82%), Total

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carbohydrate (9.74%) and fat (0.65%) were recorded in thorny cultivars as compared to thornless. Numerous investigations have been conducted on diverse species of blackberries that illustrate several distinctions among most of the examined parameters [16]. The difference in proximate composition can be attributed to different geographic location and varieties (Pellegrini et al., 2018). However, the disparities observed compared to previously published data can be ascribed to several variables. These include specific varieties, harvest time, fruit maturity and ripening, environmental and soil conditions, sunlight exposure and postharvest handling methods. These factors significantly influence the physical and chemical characteristics of fruit as reported early by [17].

Experiment: 2

Biochemical Parameters:

Results showed a statistically significant increase in pH of samples throughout storage duration. Higher pH (4.5) was noted in T0 (control) at 12 days of storage duration as compared to lower (0.89) in T3 at 3 days of storage. After 12 days of storage, higher TSS (10.5) was recorded in T3 as compared to lower (7.2) in T0 (control). In peaches and apricot studies, it was documented that higher respiration was recorded in untreated fruits as compared to treated ones. The control group exhibited a higher respiration rate, which resulted in the utilization of natural acids. Consequently, this led to a reduction in the natural acid content within the fruit, ultimately causing an elevation in pH (Diaz-Mula et al., 2009). The variations may be attributed to environmental variables, planting conditions, and the timing of berry harvest (Cho et al., 2005). According to Ramesh et al, [18], it was noted that the decrease in TSS can be attributed to the metabolic consumption of sugars during the process of respiration. According to [19], it was also documented that the presence of OA may contribute to the preservation TSS by exerting an anti-senescence effect. The anti-senescence effect leads to a reduction in respiration rate during storage, thereby decreasing the formation and consumption of metabolites (Table 5).

Consequently, this causes the retention TSS (Yaman & Bayoındırli, 2002). The research findings indicated that the blackberry variety treated with OA 1.5mM exhibited the highest retention of TSS. The retention of TSS in apricots and mangoes following treatment with organic acids (OA) has also been documented in previous studies [20]. Fruit weight loss was significantly influenced by oxalic acid treatments. An increase in fruit weight loss was noted in T0 (control) as compared to fruits treated with oxalic acid. Significantly, higher weight loss (44.3%) was recorded in T0 (control) during 12 days of storage as compared to lower (17.9) in T1 (1.5 mM OA). Blackberry fruits are prone to rapid loss of water due to their thin skin, which leads to shrinkage and degradation (Bin et al., 2014). The reduced amount of weight in samples that were treated can be ascribed to the therapeutic effects of these treatments on the stability and preservation of the integrity of cells and tissue permeability [21]. The decrease regarding the metabolic process of berries caused by treatments is also accountable for decreased weight reductions [22]. Results regarding ascorbic acid contents showed significant variations during storage duration. Maximum ascorbic acid (30.4 %) was retained after 12 days of storage in T2 as compared to minimum ascorbic acid (24.4 %) in T0 (control). The results of our study align closely based on the results of [23], who also observed a notable reduction in ascorbic acid content. The occurrence of pomegranate spoilage is recorded over the duration of preservation. The decline in ascorbic levels during storage attributed to the oxidation of dehydroascorbic acid, leading to the formation of diketogulonic acid [24] (Table 6).

Fruit firmness and TA

Among oxalic acid treatments, significant variations were observed during storage period. Maximum fruit firmness (903 gm) was retained in T1 as compared to minimum in T0 (265 gm) as presented in (table 7). Early research has also demonstrated the effectiveness of oxalic acid (OA) in preserving the firmness of apricots [25]. Similarly, [26] and [20] have reported the positive effects of OA on retaining the firmness and delaying softening in peach. Additionally, [20] have found that OA can extend the postharvest life of mango. Firming effects from oxalic acid may be due to delayed enzyme activity involved in structure of cell wall loosening, expanding and hydrolysis of polygalacturonase and pectin methyl esterase [27]. (Zheng et al .,) [20] has documented comparable findings in the case of peach. The firming effect of oxalic acid (OA) is ascribed to its ability to preserve membrane integrity, resulting in an augmentation of Cellular turgor [27]. Moreover, oxalic acid can inhibit the ACO (1-aminocyclopropane-1-carboxylic acid oxidase) activity which converts ACC to ethylene that causes decrease in firmness (Kazemi et al., 2011). TA plays a significant role in preserving fruit quality. During storage a significant decrease in TA was noted as shown in (Table 7).

There is a prevailing belief that naturally occurring acids serve as substrates for glycolysis and tricarboxylic acid cycle pathways in the process of fruit ripening (Diaz-Mula et al., 2009; Valero et al., 2011). The application of oxalic acid resulted delayed in the ripening of blackberry fruits (Gimenez et al., 2017). Additionally, it was observed that TA of the treated blackberry was greater in comparison to those that were untreated group. Comparable results have also been reported for plum treated with OA [28]. The levels of total sugars rise from the 3 days to the 12 days of storage, regardless of the treatments applied. Significantly, T1 exhibited a higher total sugar content (16.1%) as compared to lower (14%) in T0 (control). Similarly, reducing sugars were found to be more (9.45%) in T1 as compared to less (8.72) in T0 (control). Moreover, an increasing pattern was observed during storage for total sugars and reducing sugars as given in Table 8. (Baviskar et al., 1995) observed rise in sugar levels over the span of storage could potentially be attributed to alterations in metabolism occurring in soluble molecules, as well as an increased transformation of

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naturally occurring acids into sugars. (Broughton and Tan) [29] have documented this information in the custard apple fruits (Table 8).

Phytochemical Parameters:

Phytochemicals including total phenolics and total flavonoid were found to be significant in terms of treatments and storage days as described in (Table 9). Among different treatments, T3 exhibited higher (68.48) phenolics as compared to lower (61.38) in T2. However, higher total flavonoids were found to be higher (18.25%) in T1 as compared to lower (10.24%) in T0 (control). Results regarding storage duration showed decreasing patterns for different oxalic acid treatments as shown in table 9. Phytochemicals, including total phenolics and flavonoids have been identified as advantageous antioxidants and have demonstrated ROS screening capability [30]. A significant positive correlation coefficient was observed, indicating a strong relationship between the total phenolics and flavonoids content in peaches. This suggests that flavonoids play a crucial role as a subgroup of phenolic compounds in berries. (Cantin et al.,) [31] also reported higher correlation coefficients for peach and nectarine cultivars. Similar trends were observed in mango fruit [32]. Pomegranate fruit exhibited a notable decrease in the levels of total phenolics, when subjected to a temperature of 4 degrees Celsius [32,33] (Table 10).

The acceptability of blackberry is significantly influenced by skin color. The skin color of blackberry fruit was found to be significant in terms of treatments and storage duration. Significant reduction was noted in lightness (L*) over the time of storage for control and treated fruits. T1 exhibited the highest Lightness (L*) (24.64) as compared to lowest (19.52) in T0 (Control). Moreover, lightness (L*) decreased with the advancement of storage. Higher lightness (L*) was reduced from 54.05 to 19.52 in T0 from harvest to 12 days after storage. Moreover, redness (a*) was increased during storage among treatments. Significantly, redness (13.32 to 24.59) increased in T0 (control) from 3 to 12 days of storage as presented in Table 10. Oxalic acid treatment has been found to be significant for retaining original color through chlorophyll pigments (Dokhanieh et al., 2013). Additionally, the greatest b* value (37.40) was observed in T0 (control) as shown in table 11. A synergistic relationship has been observed between color pigments resulting in a dark reddish-yellow hue in blackberries and hastening the ripening process (Goncalves et al., 2004) (Table 11). Similarly, it was observed that there was a progressive increase in treated samples showcasing fluctuating a* and b* values. This increase was linked to the impact of oxalic acid on respiration rate, consequently resulting in delay of ripening process [28]. Our results are closely linked to the findings of [34] in his investigations of pomegranate [35-67].

Conclusion

This study highlights the importance of blackberries as a diverse nutritional source. Notably, physicochemical, nutraceutical and proximate analysis exhibited substantial variation between thorny and thornless blackberry cultivars. Thorny cultivar showed better performance regarding physicochemical, nutraceutical and proximate composition as compared to thornless. This study also revealed the significance of oxalic acid treatments for preservation and quality control of blackberries during the storage period. The investigation suggested that oxalic acid treatments played a pivotal role in preserving the fruit quality of blackberry. Among treatments, T1 (1.5 mM) was found to be best for maintaining the quality even after 12 days of storage period. So, from findings it was suggested that postharvest oxalic acid treatment improves the physicochemical properties of fruits by extending shelf life.

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