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FOOD TECHNOLOGY

Characterization of new late-spring-frost-tolerant apricot hybrids: physical and biochemical fruit quality attributes, volatile aroma compounds

Aliseydi Doğan[1] **Fırat Ege Karaat**[2] **Okan Levent**[3] **Bayram Murat Asma**[1*]

[1]Department of Horticulture, Malatya Turgut Ozal University, 44210, Battalgazi, Malatya, Turkey. E-mail: bayram.asma@ozal.edu.tr. *Corresponding author.
[2]Department of Horticulture, Adıyaman University, Adıyaman,Turkey.
[3]Department of Food Engineering, İnönü University, Malatya, Turkey.

ABSTRACT: Late spring frosts is one of the most important restricting abiotic stress factors of apricot growing worldwide. In this study; some physical, biochemical fruit quality characteristics and volatile aroma compounds were determined in fresh fruit samples of thirteen late spring frost tolerant apricot hybrids recently obtained from Turkish apricot breeding programme. A wide variation was reported among apricot genotypes in all of the evaluated physical and biochemical fruit characteristics and also volatile aroma compounds. Fruit size varied between 27.2 and 60.5 g, total soluble solids between 13.6 and 17.4 %, total carotene 26.6 and 42.8 (mg.100 g^{-1}), and total phenolics content 354.2 and 673.1 (GAE.100 g^{-1}). A total of 42 flavor components belonging to various flavor compound groups were identified. The main volatile aroma compound groups detected in the assessed apricot genotypes were; aldehydes, ketones, esters, alcohols, terpenes, acids, and other compounds. Among the detected compounds; Hexanal, 2-Hexenal, 1-Hexanol, 2-Hexen-1-ol, Limonene were the most abundant compounds in terms of concentration. Hexanal varied between 55.8 and 528.5 µg.kg^{-1}, and 2-Hexen-1-ol changed between 25.7 and 297.9 µg.kg^{-1} fresh weight. Correlation analysis revealed significant correlations among some aroma compounds and biochemical fruit quality characteristics. Significant correlations were reported for esters with titratable acidity (r=0.79) and total carotene (r=-0.61) and aldehydes were found as highly correlated with total soluble solids (r=-0.69). The results of the study will be beneficial in terms of food analysis, cultivation, and breeding studies of apricot.
Key words: breeding, hybridization, phytochemicals, *prunus armeniaca* L., stress tolerance.

Caracterização de novos híbridos de damasco tolerantes a geadas tardias: atributos físicos e bioquímicos de qualidade do fruto, compostos aromáticos voláteis

RESUMO: As geadas do final da primavera são um dos fatores de estresse abiótico restritivos mais importantes do cultivo de damasco em todo o mundo. Neste estudo, algumas características físicas e bioquímicas de qualidade da fruta e compostos aromáticos voláteis foram determinados em amostras de frutas frescas de 13 híbridos de damasco tolerantes à geada da primavera, recentemente obtidos do programa de melhoramento de damasco turco. Uma grande variação foi encontrada entre os genótipos de damasco em todas as características físicas e bioquímicas dos frutos avaliados e também nos compostos aromáticos voláteis. O tamanho dos frutos variou entre 27.2 e 60.5 g, sólidos solúveis entre 13.6 e 17.4 %, caroteno total 26.6 e 42.8 (mg.100 g^{-1}) e teor de fenólicos totais 354.2 e 673.1 (GAE.100 g^{-1}). Um total de 42 componentes aromatizantes pertencentes a vários grupos de compostos aromatizantes foram identificados. Os principais grupos de compostos aromáticos voláteis detectados nos genótipos de damasco avaliados foram: aldeídos, cetonas, ésteres, álcoois, terpenos, ácidos e outros compostos. Os compostos: Hexanal, 2-Hexenal, 1-Hexanol, 2-Hexen-1-ol e Limoneno foram os mais abundantes em termos de concentração. O hexanal variou entre 55.8 e 528.5 µg.kg^{-1}, e o 2-Hexen-1-ol variou entre 25.7 e 297.9 µg.kg^{-1} demassa fresca . A análise de correlação revelou correlações significativas entre alguns compostos aromáticos e características bioquímicas de qualidade do fruto. Correlações significativas foram encontradas para ésteres com acidez titulável (r=0.79) e caroteno total (r=-0.61) e aldeídos foram encontrados como altamente correlacionados com sólidos solúveis totais (r=-0.69). Os resultados do estudo serão benéficos em termos de análise de alimentos, cultivo e estudos de melhoramento de damasco.
Palavras-chave: melhoramento, hibridação, *prunus armeniaca* L., fitoquímicos, tolerância ao estresse.

INTRODUCTION

Extreme climatic events such as drought, heat waves and late spring frosts threaten sustainable agricultural production in recent years due to global climate change. In the fruit growing, late spring frost damage possibilities increase when the genotypes bloom and set fruit early (MUFFLER et al., 2016; VITRA et al., 2017). According to climate warming scenarios, it is foreseen that the growth, productivity and geographical spread of many economically important plant species will be restricted (GU et al., 2008; VITASSE et al., 2019). This is undoubtedly true for fruit species whose yield and quality characteristics

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are shaped by environmental conditions such as climate and soil (LUEDELING, 2012; NAWAZ et al., 2020).

Although, apricot is a deciduous fruit species, and frost occurrence frequency is minimized in the winter, late spring frosts can usually cause serious damages. The main problems of apricot production in the world are extreme winter and late spring frosts, poor adaptation to environmental conditions, plum pox virus disease, drought and global climate change (LEDBETTER, 2008; ASMA, 2011). Apricot, peach and some plum cultivars are often damaged by spring frosts because they bloom earlier than other fruit types. In temperate climates, spring frost is an important environmental factor that limits apricot yields, as a consequence of strong injuries to buds, flowers and developing fruits (BARTOLINI et al., 2006). Late spring frosts frequently occur in Malatya, the world's most important dried apricot production center, and serious economic losses are faced. Product losses till to 50-90% have occurred due to severe frosts as it had been confronted in 2004, 2010 and 2014 late springs (ASMA et al., 2016).

In general, the probability of frost damage differs according to the region, the level and duration of the frost, the cultivars and the physiological situation and phenological phase stage of the trees (GUERRIERO et al., 2006). In order to minimize the economic losses in apricot, many researches have been carried out on physiology (KAYA et al., 2018; DUMANOGLU et al., 2019), molecular features (NAZEMI et al., 2016; SALAZAR et al., 2016) artificial freezing tests (OZTURK et al., 2006; GUNES, 2006) and field studies (AKÇA et al., 2000; GUERRIERO et al., 2006). Obviously, the most effective method to protect from spring frosts is to breed new late-blooming apricot varieties that are cold-resistant or tolerant (DEMIRTAS et al., 2010; DOĞAN, 2018).

Natural components such as dietary fibers, phenolic compounds, organic acids, carotenoids, and sugars are of the important fruit quality elements related to the nutritional value of fruits and vegetables (GÜÇLÜ et al., 2006; AKIN et al., 2008). Thanks to their antioxidant activities these compounds scavenge free radicals and destroy their chain reactions and stabilize unstable oxygen molecules (DAI & MUMPER, 2010; CARBONE et al., 2018). Apricots are also known as a rich source of bioactive compounds, especially for polyphenols and carotenoids (ERDOGAN-ORHAN & KARTAL, 2011).

Being a mixture of various metabolites and a result of special assortment, aroma compounds play a key role in the formation of the special characteristics of many foods and beverages. Besides, these compounds strongly influence the fruit quality variation among species and cultivars. Previous studies revealed that aldehydes, esters, alcohols, terpenes and acids were the main aroma compound groups of apricot fruits, and hexanal, hexyl acetate, (Z)-3-hexenyl acetate, (E)-2-hexenyl acetate, ethanol, 1-hexanol, (Z)-3-hexenol and (E)-2-hexen-1-ol were the main detected compounds (GOKBULUT & KARABULUT, 2012; PINTEA et al., 2020).

Currently, fruit breeders mostly select new cultivars according to external fruit characteristics such as fruit weight, color, appearance and harvest time; organoleptic and nutritional characteristics are of the secondary goals. However, consumers have plenty of fruit and vegetable alternatives on the market, and fruit composition is becoming more and more important. There are very few studies on the phytochemical and aroma compounds of apricot varieties tolerant to abiotic stress conditions such as drought, late spring frosts and heat waves (NAZEMI et al., 2016; KHADIVI-KHUB & KHALILI, 2017). The knowledge about fruit quality characteristics of apricots tolerant to late spring frosts is limited, especially for biochemical attributes and volatile aroma compounds. The comparison of cultivars and obtained hybrids provide valuable support for breeding studies.

Here, the fruit quality, biochemical characteristics and aroma components of trees tolerant to spring late frosts of thirteen promising apricot genotypes obtained from Apricot Breeding Programme launched by İnönü University Apricot Research Centre in 1999. The main objectives of the study is to detect how the fruit quality attributes including physical, biochemical and aroma components change in late spring frost tolerant apricots, and compare the tolerant hybrids in relevant characteristics.

MATERIALS AND METHODS

Plant materials and experimental design

The plant materials of this study were 13 apricot hybrids characterized by late spring frost tolerance, high fruit quality, and yield obtained from the "Multi-Purpose Apricot Breeding Project", and a reference cultivar ('Kabaaşı') which was also reported as a late spring frost tolerant cultivar in previous reports (GUNES, 2006). The origin, pedigree and some phenological records of the plant material is presented in table 1. Besides, some organoleptic fruit quality characteristics of the assessed genotypes are presented in table 2.

The research was carried out at the Research and Application Orchards of İnönü

Table 1 - Origin, pedigree and some phonological records of assessed apricot genotypes.

Genotype	Origin	Pedigree	----------BI----------		---------FB---------		---------BE--------		--------RT--------	
			2016	2017	2016	2017	2016	2017	2016	2017
1-18	Turkey	Paviot × Hasanbey	06 Mar	14 Mar	11 Mar	18 Mar	16 Mar	24 Mar	06 Jun	15 Jun
2-67	Turkey	Kabaaşı × Harcot	07 Mar	16 Mar	13 Mar	20 Mar	19 Mar	26 Mar	08 Jun	22 Jun
3-42	Turkey	Roksana × Harcot	06 Mar	15 Mar	11 Mar	19 Mar	17 Mar	27 Mar	08 Jun	22 Jun
4-118	Turkey	Paviot × Kabaaşı	08 Mar	17 Mar	13 Mar	21 Mar	18 Mar	28 Mar	11 Jun	28 Jun
5-16	Turkey	Zard × Adil Cevaz	08 Mar	17 Mar	12 Mar	21 Mar	17 Mar	28 Mar	13 Jun	03 Jul
6-74	Turkey	Kabaaşı × Roksana	07 Mar	15 Mar	11 Mar	20 Mar	16 Mar	26 Mar	03 Jun	19 Jul
7-04	Turkey	Şekerpare × Stark Early Orange	07 Mar	16 Mar	11 Mar	22 Mar	16 Mar	28 Mar	21 Jun	06 Jul
2-216	Turkey	Kabaaşı × Harcot	06 Mar	14 Mar	11 Mar	18 Mar	19 Mar	23 Mar	21 Jun	04 Jul
8-34	Turkey	Hacıhaliloğlu × Stark Early Orange	09 Mar	16 Mar	13 Mar	20 Mar	17 Mar	26 Mar	27 Jun	07 Jul
9-04	Turkey	Çataloğlu × Roksana	06 Mar	15 Mar	12 Mar	20 Mar	18 Mar	26 Mar	27 Jun	19 Jul
10-06	Turkey	Paviot × Mahmutun Eriği	08 Mar	17 Mar	12 Mar	22 Mar	17 Mar	28 Mar	27 Jun	06 Jul
11-35	Turkey	Sakıt × Alyanak	07 Mar	15 Mar	13 Mar	21 Mar	18 Mar	28 Mar	01 Jul	07 Jul
12-01	Turkey	Şekerpare × (Geç Aprikoz × Sakıt-1)	07 Mar	16 Mar	12 Mar	20 Mar	17 Mar	25 Mar	01 Jul	01 Jul
Kabaaşı	Turkey	Chance Seedling	06 Mar	13 Mar	10 Mar	17 Mar	16 Mar	23 Mar	05 Jul	12 Jul

BI: Blooming Initiation, FB: Full Blossom, BE: Blooming Ending, RT: Ripening Time.

University located in Malatya Province of Turkey. Trees of the hybrids evaluated as part of the study were planted in a 3 × 1.5 m and the cultivars in a 5 × 5 m grid, and Zerdali seedlings were used as rootstocks. The trees were subjected to standard cultural practices including drip irrigation and fertigation. There were no significant negative impacts of water stress, nutrient deficiency or pests and diseases that would affect the results, and in order to evaluate environmental impacts the study was performed across two consecutive years (2016 and 2017). All of the observations, measurements and analyses were performed on the fruit samples collected from outer canopy layer of each genotype.

Physical and biochemical fruit quality traits

Collected fruit samples, 25 fruits from each replicate, were evaluated for some physical and biochemical fruit quality traits. Fruit weight (FW) and kernel weight (KW) values were measured using a precision scales (Ohaus PAJ 812 CM 0.01 g, Germany) and expressed in grams, and flesh/kernel rate (F/K) was calculated by division of these values and expressed in percentage. Flesh firmness (FF) was measured by a manual penetrometer (Akyol GY-3, Turkey) and expressed as $kg.cm^{2-1}$.

As part of biochemical fruit quality attributes, the contents of total soluble solids (TSS), titratable acidity (TA), total carotene (TC), and total phenolics (TP) were determined. TSS and TA percentages were measured on the homogenized fruit juice extracted from the sample fruits. TSS was measured via manual refractometer (Greinorm 0–32 Brix, Germany). TA was detected according to the method reported by HAFFNER & VESTRHEIM (1996) and expressed as the malic acid (%). The maturity index (TSS/TA rate) was calculated by division of these values.

The total amount of TC was determined by modifying the method applied by AKIN et al. (2008). Fruit samples (5 g from each genotype) were mixed with 20 ml of petroleum ether-methanol (90:10) solvent, and homogenized in 13600 rpm for 5 minutes, and mixed with 10 ml diluted water and vortexed for 30 seconds. The mixture than centrifuged in 6000 rpm for 4 minutes, the pellet were mixed with 7.5 ml of petroleum ether-methanol, and homogenized in 13600 rpm for 1 minute, and centrifuged again in 6000 rpm for 4 minutes. The obtained extract was filtered and absorbance values were read at 450 nm (Shimadzu UV-1800, Kyoto, Japan), and TC values were calculated based on the calibration curve obtained using carotene standard prepared in the range of 5-100 ppm and the results are given in milligrams of TC equivalents per 100 g of fruit sample ($mg.100g^{-1}$).

TP value was measured according to Folin-Ciocalteu spectrophotometric method described by SINGLETON et al. (1999) using 2% (w/v) Na_2CO_3

Table 2 - Sensorial fruit quality characterization of apricot cultivars and hybrids subjected to assessments.

Genotype	Fruit Shape	Skin Color	Flesh Color	Over Color	Kernel Shape	Kernel Taste	Attractiveness	Fruit Taste
1-18	Flat Round	Light Orange	Orange	Very Low	Elliptical	Sweet	Good	Sour
2-67	Oval	Light Orange	Orange	Moderate	Oval	Sweet	Very Good	Moderate
3-42	Round	Yellow	Orange	Low	Oval	Sweet	Good	Moderate
4-118	Oval	Orange	Orange	Low	Oval	Sweet	Good	Moderate
5-16	Oval	Yellow	Yellow	Very Low	Elliptical	Sweet	Good	Sour
6-74	Flat Round	Light Orange	Orange	Moderate	Oval	Sweet	Very Good	Moderate
7-04	Oval	Light Orange	Light Orange	Moderate	Oval	Sweet	Good	Moderate
2-216	Flat Round	Light Orange	Light Orange	Moderate	Elliptical	Sweet	Good	Moderate
8-34	Oval	Light Orange	Light Orange	Moderate	Oval	Sweet	Very Good	Moderate
9-04	Flat Round	Light Orange	Light Orange	Moderate	Round	Bitter	Good	Sour
10-06	Oval	Light Orange	Light Orange	Low	Oval	Sweet	Good	Moderate
11-35	Round	Cream	Cream	Low	Oval	Sweet	Good	Moderate
12-01	Flat Round	Light Orange	Light Orange	High	Oval	Bitter	Good	Moderate
Kabaaşı	Oval	Yellow	Yellow	Moderate	Oval	Sweet	Good	Sweet

(water) and Folin-Ciocalteu reagent. In this context, 5 g fruit sample were mixed with 25 ml of methanol containing 0.1% HCl and kept in the freezer at -18°C for 24 hours. The mixture (40 µL) was mixed with 200 µL of Folin-Ciocalteu reagent, vortexed for 1 minute, kept in the dark for 5 minutes, mixed with 600 µL of 2% Na_2CO_3 and the obtained samples were read at 765 nm (Shimadzu UV-1800, Kyoto, Japan) after keeping in the dark for 120 minutes. A calibration curve formed by reading of gallic acid solutions prepared at different concentrations (50-1000 ppm) was used to calculate the results which were expressed as milligrams of gallic acid equivalents (GAE) per 100 g fruit sample (GAE.100g^{-1}).

Volatile aroma compounds

Sample preparation and SPME conditions

Volatile aroma compound contents of apricot fruit samples were detected by SPME with a Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) (50/30 µm coating thickness; 2 cm length; Supelco, Bellefonte, PA, USA) fiber. A 3 g of the homogenized sample in triplicate was immediately transferred into 15 mL of SPME vials (Supelco, Bellefonte, PA, USA) within 2 min, followed by 10 µL of internal standard containing 81 mg/kg of 2-methyl-3-heptanone (all organic volatile compounds except acids) and 2-methyl-pentanoic acid (for organic volatile acids; Sigma-Aldrich Co., USA) in methanol as internal standard. Vials were placed on a heater at 40 °C for 30 min to accumulate the volatiles up to head space. Subsequently, fiber was injected in vial to absorb volatile compounds for 30 min. Desorption temperature was 250 °C MS sampler.

GC-MS conditions

Desorption of the extracted volatiles was carried out on a Shimadzu GC-2010 gas chromatography-QP-2010 mass spectrometry system (Shimadzu Corporation, Kyoto, Japan). Separation was achieved with DB-Wax column (60 m × 0.25 mm × 0.25 mm; J&W Scientific, Folsom, CA, USA). The volatile compounds were identified by retention index (RI), using an n-alkane series (C10-C26) under the same conditions. WILEY 8 and NIST 05 mass spectral libraries used to identify peaks.

Statistical analysis

All of the samples were prepared, and all of the measurements and analyses were performed with three replications in a randomized block design experiment. The obtained data were evaluated according to Duncan's Multiple Range Test. Pearson's Correlation Test were applied to analyze correlations among the physical and biochemical fruit quality characteristics and aroma groups. Besides, in order to assess the differences among the volatile aroma compounds of the genotypes, the unweighted pair-group average method (UPGMA) analysis was applied with the squared Euclidean distance. All of the statistical analyses were performed at the significance level of $P \leq 0.05$ using 'IBM SPSS Statistics 22 for Windows' software package.

RESULTS

Physical and biochemical fruit quality traits

The physical and biochemical fruit quality of the hybrids and the reference cultivar were evaluated in two consecutive years and the average values of the results obtained in two years are presented in table 3. Significant differences and large variation were obtained among the hybrids and the reference cultivars in all of the assessed fruit quality traits.

When the results of the years were compared, the results of the first study year were significantly higher than that of the second probably because of the crop-load differences between the years which was lower in the first year. However, the impact of the years did not change the results when comparing the genotypes. For that reason, the year effect was ignored by pooling the data of 2016 and 2017. The main reason for the differences in the crop-load between years is thought to be related to the occurrence of more severe late spring frosts in 2016 compared to 2017, and the greater frost damage to flowers and fruits in 2016 due to these frosts. While severe frosts such as -5.7 °C and -5.3 °C occurred in 2016, especially during the flowering period, moderate frosts occurred in 2017 (Table 4).

As part of weight parameters; FW, KW, and F/K were measured and evaluated. FW was found as the lowest in ‘2-216’ with 27.2 g and the highest fruit weight was found in ‘10-06’ with the value of 60.5 g. Conversely, the reference cultivar ‘Kabaaşı’ was the genotype presenting the lowest average KW value with 2.2 g, while ‘11-35’ gave the highest KW value (3.8 g). F/K values varied between 8.1 (‘5-16’) and 16.9 (‘3-42’) %. In terms of fruit flesh firmness, it was determined that the assessed hybrids had higher values than the reference cultivar and the genotype ‘6-74’ had the hardest fruits with the value of 8.6 kg.cm$^{2-1}$. On the other hand, the lowest value was obtained in ‘1-18’.

The highest TSS content was measured in the reference cultivar ‘Kabaaşı’ (21.5 %), while in the

Table 3 - Physical and chemical fruit quality properties of apricot cultivars and hybrids subjected to assessments.

Genotype	FW (g)	KW (g)	F/K (%)	FF (kg.cm$^{2-1}$)	TSS (%)	TA (%)	TSS/TA	βC (mg.100g^{-1})	TP (GAE.100g^{-1})
1-18	43.6 ± 11.5 a-e	3.3 ± 0.5 abc	12.0 ± 1.9 e	5.3 ± 3.5 ef	13.6 ± 2.2 bc	1.2 ± 0.1 bc	11.6 ± 1.2 de	39.5 ± 1.5 bc	569.5 ± 6.6 c
2-67	37.4 ± 15.7 b-e	2.4 ± 0.6 def	14.0 ± 3.1 cde	7.9 ± 1.0 ab	17.4 ± 3.4 ab	1.2 ± 0.6 bc	16.5 ± 5.7 abc	34.5 ± 1.6 ef	437.9 ± 15.6 e
3-42	57.4 ± 21.2 a	3.1 ± 0.5 abc	16.9 ± 3.7 ab	7.5 ± 0.4 abc	14.5 ± 2.6 bc	1.1 ± 0.5 bc	14.7 ± 3.7 bcd	28.2 ± 0.9 hi	354.2 ± 20.3 g
4-118	38.6 ± 15.5 b-e	2.6 ± 0.8 c-f	13.4 ± 1.6 cde	6.8 ± 0.7 a-f	14.8 ± 1.6 bc	1.1 ± 0.1 bc	13.5 ± 1.1 b-e	34.1 ± 1.5 ef	489.2 ± 5.8 d
5-16	29.4 ± 12.8 de	3.1 ± 0.8 abc	8.1 ± 1.8 f	6.2 ± 1.7 b-f	16.6 ± 3.9 ab	2.2 ± 0.3 a	7.4 ± 0.6 f	26.6 ± 1.6 i	381.3 ± 20.4 fg
6-74	46.6 ± 21.2 a-d	3.0 ± 0.7 a-d	14.1 ± 2.8 b-e	8.6 ± 0.9 a	11.4 ± 4.8 c	1.2 ± 0.4 bc	9.4 ± 0.6 ef	36.7 ± 0.8 cde	562.5 ± 18.4 c
7-04	44.1 ± 11.9 a-e	3.3 ± 0.7 abc	12.4 ± 0.7 de	7.0 ± 0.5 a-e	15.7 ± 4.2 bc	1.4 ± 0.2 b	11.4 ± 1.5 de	39.9 ± 1.4 b	584.3 ± 36.7 c
2-216	27.2 ± 10.6 e	2.9 ± 0.6 b-e	8.6 ± 1.4 f	5.0 ± 0.3 f	16.7 ± 5.0 ab	1.0 ± 0.3 bc	16.4 ± 0.8 abc	32.5 ± 1.7 fg	375.1 ± 19.7 fg
8-34	53.9 ± 8.5 ab	3.2 ± 0.1 abc	15.9 ± 2.0 abc	7.5 ± 0.8 abc	15.1 ± 5.6 bc	1.2 ± 0.1 bc	13.1 ± 6.1 cde	36.2 ± 1.3 de	559.4 ± 13.2 c
9-04	48.5 ± 12.1 abc	2.7 ± 0.4 c-f	17.3 ± 1.9 a	5.9 ± 1.0 c-f	15.2 ± 3.5 bc	1.2 ± 0.1 bc	12.6 ± 2.4 cde	38.9 ± 1.7 bcd	622.7 ± 32.2 b
10-06	60.5 ± 16.0 a	3.6 ± 0.5 ab	15.7 ± 2.0 abc	7.3 ± 0.8 a-d	16.7 ± 4.0 ab	0.9 ± 0.2 c	17.5 ± 0.9 ab	42.8 ± 2.9 a	673.1 ± 26.0 a
11-35	47.3 ± 9.8 a-d	3.8 ± 0.2 a	11.6 ± 2.6 e	5.6 ± 2.4 def	14.7 ± 4.7 bc	1.1 ± 0.1 bc	14.4 ± 6.2 bcd	41.3 ± 2.5 ab	635.9 ± 7.5 b
12-01	34.4 ± 1.7 cde	2.3 ± 0.1 ef	14.1 ± 0.9 b-e	6.8 ± 0.8 a-f	16.6 ± 2.9 ab	0.9 ± 0.0 c	17.5 ± 3.5 ab	30.0 ± 0.2 gh	399.5 ± 15.5 f
Kabaaşı	33.0 ± 4.7 cde	2.2 ± 0.1 f	15.2 ± 1.6 a-d	6.8 ± 0.4 a-f	21.5 ± 2.2 a	1.1 ± 0.1 bc	19.5 ± 1.2 a	39.5 ± 1.5 bc	569.5 ± 6.6 c

FW: Fruit Weight, KW: Kernel Weight, TSS: Total Soluble Solids, TA: Titratable Acidity, FF: Flesh Firmness, F/K: Flesh/Kernel Rate, TC: Total Carotenoids, TP: Total Phenolics
The values given with “±” indicate the Standard Deviations. The differences between the values signed with different letters are significant at $P < 0.05$ significance level.

Table 4 - Spring late frosts recorded at the study area in 2016 and 2017.

---------------2016---------------		------------2017------------	
Date	Degree (°C)	Date	Degree (°C)
17 Mar	-2.8	06 Mar	-4.0
18 Mar	-5.7	07 Mar	-3.1
19 Mar	-5.3	08 Mar	-1.1
21 Mar	-4.4	09 Mar	-0.7
22 Mar	-3.2	15 Mar	-0.8
23 Mar	-0.7	16 Mar	-1.5
30 Mar	-0.4	18 Mar	-3.3
31 Mar	-1.9	19 Mar	-2.9
01 Apr	-0.1	23 Mar	-2.7
02 Apr	-0.4	24 Mar	-1.8
		25 Mar	-2.9
		29 Mar	-1.3
		30 Mar	-0.6
		04 Apr	-0.8
		10 Apr	-1.1
		11 Apr	-0.2
		12 Apr	-1.8
		26 Apr	-0.7

hybrids the genotype '2-67' was found as having the highest TSS value (17.4 %). The lowest TSS value (11.4 %) was found in '6-74'. The obtained TSS/TA ratio values changed between 7.4 ('5-16') and 19.5 ('Kabaaşı'). The maturity index values were reported in accordance with the sensorial fruit taste characteristics of the assessed genotypes described in table 2. The highest TSS/TA value was found in the reference cultivar 'Kabaaşı' and the fruit taste was scored as 'Sweet', while the genotypes '5-16' which was scored as 'Sour' presented the lowest maturity index.

In order to evaluate the bioactive compound potential of the late spring frost tolerant apricot hybrids examined as part of the study, the contents of TC and TP were detected and evaluated (Table 3). The amount of TC in the apricot genotypes varied between 28.2 and 42.8 mg.100g^{-1}. The lowest and highest TC values were found in '3-42' and '10-06', respectively. In terms of TP, the lowest values found was 354.2 GAE.100g^{-1} ('3-42), whilr 673.1 GAE.100g^{-1} ('10-06') was the highest value.

Volatile aroma compounds

Concentrations of the volatile compounds in thirteen apricot genotypes are given in table 5. A total of 42 volatiles were identified in the apricot samples including 10 aldehydes, 5 ketones, 9 esters, 7 alcohols, 5 terpenes, 2 acids and 4 other compounds.

Among aldehydes; hexanal and 2-hexanal found abundantly in all apricot samples. 2-hexanal concentrations changed between 0 and 528.50 µg.kg^{-1} FW in '7-04' and '6-74', respectively. In the determined ketones; 6-Methyl-5-hepten-2-one in '1-18' (1.21 µg.kg^{-1} FW) and β-Ionone in '10-06' (1.73 µg.kg^{-1} FW) were the ones which found in the highest concentrations. Total concentrations of alcohols varied from 52.99 µgkg^{-1} FW ('2-216') to 403.37 µg.kg^{-1} FW ('3-42'). Seven alcohol compounds (Ethanol, 1-butanol, 1-pentanol, 1-hexanol, 3-hexanol, 2-Hekzen-1-ol and linalool) were determined in apricot samples. Concentrations of the esters were in the range of 1.02 and 31.01 µg/kg^{-1} FW in '1-18' and '5-16', respectively. The principal esters were (*Z)*-3-Hexenyl acetate (0 to 15.07 µg.kg^{-1} FW), Hexyl acetate (0 to 9.75 µg.kg^{-1} FW) and (*E)*-2-Hexenyl acetate (0.12 to 3.35 µg.kg^{-1} FW) in apricot samples. In terms of acids and other aroma compounds, 2-Methyl-propanoic acid and 2-Methyl-butanoic acid were only detected in '2-67', '3-42' and '5-16' samples. Aromatic hydrocarbons, such as toluene and tert-butyl-benzene and one hydrocarbon (decane) were identified in apricot samples. Total concentration of decane varied between 0.37 ('4-118') and 1.23 µg.kg^{-1} FW ('10-06').

Cluster analysis

The frost tolerant hybrids evaluated in this study were subjected to cluster analysis and classified based on the volatile aroma compound concentrations (Figure 1). According to the results, the assessed hybrids were distributed in three main clusters. The hybrid '6-74' formed the third cluster alone which was especially separated from the other genotypes with high contents of Hexanal, 2-Hexanal; and consequently, total concentrations of Aldehydes. The hybrids '1-18', '3-42', '8-34', and '9-04' constituted the second cluster.

Correlations

Correlations among aroma groups and other assessed fruit quality traits were analyzed and obtained correlation coefficients are presented in table 6. Results indicated significant correlations among some of the characters. High correlations between Aldehydes and TSS (r=-0.69) were obtained in negative way. Esters were found highly correlated with TA (r=0.79) and TC (r=-0.61). FW and KW were moderately correlated with TP (r=0.59 and r=0.56, respectively). Besides, a very high positive correlation was detected between TP and TC, as expected. Other expected correlations were found between KW and F/K (r= 0.78), and TA and TSS/TA (r=-0.80).

Table 5 - Average concentrations (µg.kg-[1] fresh weight) of volatile compounds identified in apricot hybrids.

Compound	RI	1-18	2-67	3-42	4-118	5-16	6-74	7-04	2-216	8-34	9-04	10-06	11-35	12-01
----Aldehydes----														
2-Methylbutanal	910	nd	0.24	0.30	0.15	0.47	0.28	0.02	0.24	0.11	0.09	0.08	0.05	0.23
3-Methylbutanal	914	0.10	0.10	0.07	0.13	0.22	0.09	0.03	0.13	0.06	0.04	0.05	0.06	0.07
Hexanal	1082	8.68	1.66	5.99	3.78	5.17	20.13	3.76	1.11	13.04	20.74	4.41	6.38	6.16
4-Pentenal	1130	nd	nd	nd	nd	nd	0.26	0.04	nd	0.12	0.17	nd	0.04	0.05
Heptanal	1185	nd	0.03	0.03	0.10	0.06	0.08	0.04	0.01	0.06	0.06	0.07	0.06	0.04
(*E*)-2-Hexenal	1204	0.34	0.19	0.67	0.57	nd	1.21	5.63	0.90	0.71	0.82	0.20	0.19	0.20
2-Hexenal	1225	262.30	160.80	294.30	71.90	133.50	528.50	nd	55.80	336.30	397.32	144.40	145.10	181.10
Nonanal	1397	nd	nd	nd	nd	nd	nd	nd	0.03	nd	0.03	nd	nd	nd
2-Octenal	1439	0.04	nd	nd	0.07	nd	nd	nd	nd	0.04	0.06	nd	nd	nd
Benzaldehyde	1543	0.11	nd	0.08	0.10	0.07	0.06	0.12	nd	nd	0.04	nd	0.07	nd
Total		271.57	163.02	301.44	76.80	139.49	550.61	9.64	58.22	350.44	419.35	149.21	151.95	187.85
----Ketones----														
2,3-Butandione	970	nd	0.11	0.06	nd	nd	0.01	nd	nd	0.01	nd	nd	0.06	nd
3-Hydroxy-2-butanone	1291	nd	nd	nd	0.06	nd	nd	nd	nd	nd	nd	nd	nd	nd
6-Methyl-5-hepten-2-one	1352	1.21	0.50	0.92	0.70	0.58	0.57	0.36	0.52	0.52	0.53	0.85	0.23	0.19
β-Ionone	1965	nd	0.51	0.34	0.11	nd	0.08	0.57	0.24	0.78	1.52	1.73	nd	0.18
γ-Decalactone	2181	nd	nd	nd	1.27	1.01	nd	0.77	nd	nd	nd	nd	nd	nd
Total		1.21	1.12	1.32	2.14	1.59	0.66	1.70	0.76	1.31	2.05	2.58	0.29	0.37
----Esters----														
Ethyl acetate	894	0.04	0.06	0.06	1.79	1.39	0.08	0.07	0.37	nd	nd	0.13	0.35	0.08
Methyl propaonate	905	0.09	0.09	0.14	0.19	0.14	0.08	0.07	0.21	nd	0.09	0.16	0.12	0.14
Methyl butanoate	978	0.29	0.32	0.31	0.40	0.39	0.20	0.20	0.62	0.19	0.21	0.47	0.28	0.32
Ethyl butanoate	1035	nd	nd	nd	0.13	nd	nd	nd	nd	nd	nd	nd	nd	nd
Butyl acetate	1071	0.20	0.78	2.37	3.24	0.87	0.13	0.10	1.02	0.53	0.17	0.02	0.74	0.07
Butyl butanoate	1220	nd	nd	nd	0.26	0.05	0.02	0.04	nd	0.06	nd	0.06	nd	nd
Hexyl acetate	1275	0.13	nd	3.99	3.65	9.75	0.59	0.77	nd	1.17	1.37	0.35	3.11	0.93
(*Z*)-3-Hexenyl acetate	1314	0.10	0.12	3.11	0.99	15.07	0.37	0.36	1.10	1.06	1.42	nd	4.07	1.29
(*E*)-2-Hexenyl acetate	1334	0.17	0.13	1.49	0.97	3.35	0.42	0.43	1.14	0.44	0.88	0.12	0.70	0.78
Total		1.02	1.50	9.98	11.62	31.01	1.89	2.04	4.46	3.45	3.26	1.31	9.37	3.61
----Alcohols----														
Ethanol	926	0.04	0.09	0.04	5.59	2.75	0.04	0.20	0.91	nd	0.11	0.46	1.18	0.19
1-Butanol	1149	nd	0.14	nd	nd	nd	nd	nd	0.04	nd	nd	nd	nd	nd
1-Pentanol	1245	nd	nd	0.03	0.05	nd	0.04	nd	nd	0.02	nd	nd	0.04	0.04
1-Hexanol	1354	87.60	18.70	97.00	62.60	145.70	85.00	50.70	26.00	69.90	123.50	110.10	130.90	107.70
3-Hexanol	1386	2.55	1.15	5.16	0.89	8.08	2.05	0.62	0.24	3.80	3.56	1.51	7.94	1.99
2-Hexen-1-ol	1405	200.20	96.90	297.90	83.50	133.60	145.40	86.60	25.70	117.30	186.10	92.70	172.50	149.50
----Table 5 continued----														
Linalool	1547	1.16	3.02	3.24	0.79	0.89	1.63	1.17	0.10	0.36	0.90	0.40	0.50	0.25
Total		291.91	120.01	403.37	153.42	291.02	234.16	139.29	52.99	191.38	314.17	205.17	313.06	259.67
----Terpenes----														
α-Pinene	1024	0.22	nd	0.11	0.21	nd	0.18	0.05	nd	0.16	0.17	0.18	0.17	nd
Sabinene	1125	0.06	0.03	0.04	0.05	0.05	nd	0.04	0.04	0.03	nd	0.08	0.05	0.03
β-Myrcene	1157	0.10	0.28	0.32	0.17	0.29	0.32	0.27	0.32	0.33	0.26	0.49	0.30	0.19
Limonene	1195	13.51	12.01	13.33	16.08	14.31	16.14	12.01	14.12	14.29	13.61	16.77	13.96	10.16
β-Phellandrene	1212	nd	nd	0.05	nd	nd	nd	0.06	0.05	nd	nd	0.09	0.05	nd
Total		13.89	12.32	13.80	16.51	14.65	16.64	12.43	14.53	14.81	14.04	17.61	14.53	10.38
----Acids----														
2-Methyl-propanoic acid	1568	nd	nd	nd	nd	0.03	nd	nd	nd	nd	nd	nd	nd	nd
2-Methyl-butanoic acid	1663	nd	1.95	1.49	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Total		0.00	1.95	1.49	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
----Other compounds----														
Decane	1001	0.61	0.64	0.92	0.37	1.04	0.63	0.58	1.07	0.39	0.74	1.23	0.56	0.65
Toluene	1040	0.11	0.08	0.10	0.06	0.09	0.08	nd	nd	0.05	0.05	0.06	nd	0.06
2-Methyl-tetrahydrofuran	1259	nd	nd	nd	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd
Tert-butyl-benzene	1278	nd	0.22	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Total		0.72	0.94	1.02	0.44	1.13	0.71	0.58	1.07	0.44	0.79	1.29	0.56	0.71

RI: Retention Index, nd: not detected.

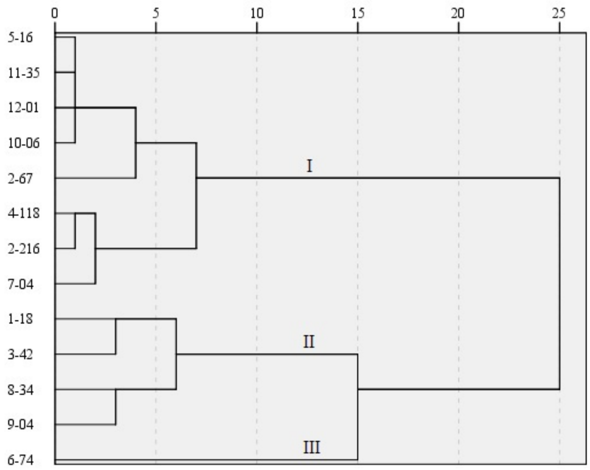

Figure 1 - Dendrogram obtained from cluster analysis based on concentrations of the identified volatile compounds.

DISCUSSION

The weight parameters are of the important fruit quality measures, and especially FW and consequently the fruit sizes playing key role on the market quality by affecting the fruit attractiveness and the preference of the consumers (LOPEZ & DEJONG, 2007). The previous studies demonstrated a large variability among the late spring frost tolerant apricot genotypes in terms of weight parameters. The FW and KW results were similar to the values of the genotypes in the clonal selection study of 'Kabaaşı' apricot cultivar conducted by AKÇA & ASMA (1997), and the researchers reported that there was a large variation in the promising genotypes they examined, especially in KW. BOSTAN et al. (1995) reported that FW in selected genotypes varied between 26.7 g and 78.7 g in their study on selection breeding wild apricots in Darende district of Malatya province, where late spring frosts are effective. In another study on selection of apricots having good fruit quality and resistance to late spring frosts, FW and KW varied between 25.3 and 50.6 g, and 2.3 and 4.2 g, respectively (AKCA & SEN, 1999).

The firmness of the fruit flesh is of great importance for marketing since the fruits having higher firmness are more tolerant to the damages occur during transportation and storage while the table apricots are delivered to the consumer and their shelf life is usually longer (CRISOSTO et al., 2001). Although, fruit flesh is a genetic feature, it is known that early or late harvesting of fruit is the most important factor affecting this feature.

TSS and TA contents are also among the most important fruit quality attributes that plays a determinant role in acceptability of the fruits by consumers. This role is called as the maturity index (the rate of TSS/TA) which is accepted as a descriptive parameter of fruit taste, and selecting genotypes of fruit species for specific uses (POLAT & CALISKAN, 2008; SUSZEK et al., 2017). For that reason, higher TSS and lower TA content in the fruits are desired characters in apricot breeding studies. In this study, the TSS and TA results were found between the limit values reported by BOSTAN et al. (1995) and ŞEN et al. (1995). Conversely, higher and lower values were obtained in TSS content when compared to the studies conducted by AKÇA & ASMA (1997), and AKÇA & ŞEN (1999), respectively.

TC and TP contents were reported in accordance with the values of AKİN et al. (2008). Furthermore, KARAAT & SERÇE (2019) reported similar TP content for 'Kabaaşı' apricot cultivar. In this study, some late spring frost tolerant hybrids presented higher values than the reference cultivar indicating that the fruits of these genotypes would be a significant source of bioactive compounds which play key roles in reducing the risk of chronic human diseases due to their antioxidative effects, and consequently high contents of bioactive compounds has been a desired fruit quality constituent and an important goal in fruit breeding studies (LIU, 2003; SERÇE et al., 2008).

In all apricot samples, 6-Methyl-5-hepten-2-one was the abundant ketone which was reported as

Table 6 - Correlations among aroma groups and other assessed fruit quality traits.

	Ketones	Esters	Alcohols	Terpenes	Acids	Other	FW	KW	F/K	FF	TSS	TA	TSS/TA	TC	TP
Aldehydes	-0.14	-0.23	0.48	0.20	0.01	-0.12	0.43	-0.06	0.54	0.39	-0.69**	-0.08	-0.31	0.06	0.21
Ketones		0.09	-0.07	0.46	-0.07	0.24	0.36	0.09	0.31	0.10	0.20	0.14	-0.08	0.23	0.31
Esters			0.29	0.11	-0.06	0.22	-0.37	0.06	-0.51	-0.19	0.17	0.79**	-0.50	-0.61*	-0.44
Alcohols				-0.06	0.07	0.05	0.43	0.25	0.34	-0.03	-0.38	0.16	-0.26	-0.14	0.05
Terpenes					-0.31	0.15	0.37	0.45	0.04	0.13	-0.37	-0.01	-0.21	0.32	0.41
Acids						0.29	0.09	-0.32	0.28	0.41	0.23	-0.06	0.30	-0.33	-0.44
Other							-0.03	0.07	-0.15	-0.05	0.44	0.14	0.20	-0.24	-0.28
FW								0.51	0.78**	0.41	-0.34	-0.36	0.13	0.50	0.59*
KW									-0.13	-0.19	-0.25	0.09	-0.20	0.53	0.56*
FK										0.54	-0.21	-0.50	0.30	0.25	0.33
FF											-0.22	-0.07	-0.02	-0.07	0.01
TSS												0.08	0.51	-0.22	-0.31
TA													-0.80**	-0.38	-0.22
TSSTA														0.11	-0.07
TC															0.94**

**. Correlation is significant at the 0.01 level *. Correlation is significant at the 0.05 level.
FW: Fruit Weight, KW: Kernel Weight, TSS: Total Soluble Solids, TA: Titratable Acidity, FF: Flesh Firmness, F/K: Flesh/Kernel Rate, TC: Total Carotenoids, TP: Total Phenolics.

a degradation product of lycopene in previous studies (WACHE et al., 2002). *γ*-Decalactone was reported as an important aroma compound of apricot and was even suggested to be responsible for the fruit sensory properties of apricot (GREGER & SCHIEBERLE, 2007). However, this ketone was not detected in most of the apricot genotypes examined as part of this study. Limonene was the most abundant terpenes detected in all apricot samples. This terpene has been reported to be responsible for fruity and citrus characters (GUILLOT et al., 2006).

As reported in the previous studies large variations are expected among the apricot genotypes even though they are grown in the same environmental conditions, and harvested in the similar ripening stage (GOKBULUT & KARABULUT, 2012). There was no accordance observed in cluster analysis results and sensorial fruit taste classifications. Thus the hybrids having sour fruit taste took place in different clusters.

Clarification of interactions among fruit characteristics via correlation analyzes brings useful practical knowledge for consumer food preferences and also for breeding studies aiming those preferences. Most of the correlations on physical and biochemical fruit quality traits presented in this current study were in accordance together with some opposite results and additional correlations reported by the previous studies (CALİSKAN et al., 2012; KARAAT & SERÇE, 2019; ÇUHACI et al., 2021). The variation among the reported results would probably be caused from the genotypic and environmental conditions. As far as we know, this study presents the first report on the correlations among aroma compounds and fruit quality parameters in assessed apricot hybrids. The obtained results indicated some significant correlations for aldehydes (with TSS) and esters (with TA and TC).

CONCLUSION

Late spring frost damages, one of the most restricting factor of apricot growing, can be significantly reduced by breeding tolerant or resistant plant genotypes. Studies on the breeding of new late spring frost tolerant apricot hybrids and analysis of fruit quality characteristics, especially bioactive compounds and aroma volatiles are limited. In this study, promising findings were obtained related to fruit quality characteristics and especially aroma compounds in new apricot genotypes tolerant to late spring frosts. All of the evaluated fruit quality characteristics varied significantly among the late spring frosts tolerant apricot genotypes assessed within the scope of the study. Especially, the hybrids '8-34' and '10-06' were found to be advantageous due to their tolerance and fruit quality characteristics. As a result of the study, the relationships between fruit quality characteristics and aroma components were also examined and a significant correlation was found between aldehydes and ketones and some biochemical fruit quality characteristics. The results of the study revealed important data regarding the fruit characteristics of apricot genotypes tolerant to spring late frosts.

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DECLARATION OF CONFLICT OF INTEREST

The authors declare that there is no conflicting interest to be disclosed.

AUTHORS' CONTRIBUTIONS

Conceptualization: BMA, and AD. Data acquisition: BMA, AD, FEK, and OL. Design of methodology and data analysis: BMA, FEK, AD, and OL. BMA and FEK prepared the draft of the manuscript. All authors critically revised the manuscript and approved of the final version.

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