EVALUATION OF A LARGE APRICOT GERMPLASM COLLECTION FOR FRUIT SKIN AND FLESH ACIDITY AND ORGANIC ACIDS COMPOSITION

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HIGHLIGHTS

- Acidity and organic acids content varied widely in apricot germplasm.
- Malate, citrate and succinate were the most abundant organic acids.
- Organic acid profiles were consistent between fruit flesh and skin of each accession.
- The large phenotypic diversity may be useful for breeding novel varieties.

ABSTRACT

Consumers continuously report a lack of taste in many apricot cultivars currently available on the market, highlighting the necessity of renewing the apricot varietal landscape grown worldwide. Sugars and acids content largely affect sweetness and aroma perception, being an important driving factor of consumers' preferences and purchase. In this work, a large apricot germplasm collection of 164 accessions was evaluated for several fruit organoleptic attributes: maturity date, fresh fruit weight, flesh firmness, soluble solids content, titratable acidity and organic acid content separated for fruit flesh and skin and dry matter. A major focus was reserved to ten organic acids (cis-aconitate, citrate, fumarate, galacturonate, malate, oxalate, quinate, shikimate, succinate and tartrate) composition in both flesh and skin tissues, quantified by HPLC technique coupled to UHPLC-HRMS. Malate, citrate and succinate were the most abundant, accounting for 98.5 % and 97.2 % of the total organic acids in fruit flesh and skin, respectively. The tested accessions showed consistent fruit acidity contents and almost similar organic acids profiles between flesh and skin, albeit some exceptions of acidity higher in flesh than in skin -and *viceversa*- occurred. This work highlights an extremely large diversity in apricot germplasm, representing a valuable genetic resource to be long term preserved and exploited in new fruit-quality oriented breeding programs. Also, a better understanding of phenotypic diversity will help the characterization of apricot accessions and a more effective management of germplasm for selecting phenotypes with improved taste.

INTRODUCTION

Despite the availability of molecular tools for selecting novel or fruit quality-improved accessions, apricot (*Prunus armeniaca* L.) market relies on a relative narrow range of cultivars (Bassi and Audergon, 2006). Fruit quality phenotyping remains the bottleneck in apricot breeding programs, one of the most delicious temperate species grown since antiquity (Faust *et al*., 1998). Apricot trees set fruits that are extremely versatile, being consumed fresh, dried or canned as jam and juice. Apricot cultivation in the Mediterranean area accounts for more than a half of the worldwide production, with a 12 % increase of EU cultivated areas between 2012 and 2017 (Eurostat, 2019).

Tree growth, fruit load, orchard management, harvest time, long-distance shipment and post-harvest handling crucially influence the final apricot quality (Audergon *et al*., 1991*a*; Audergon *et al*., 1991*b*; Laurens *et al*., 2000; Pérez-Pastor *et al*., 2007; Muzzaffar *et al*., 2018). Despite relevant improvements of outward appearance and shelf-life (mainly colour, size and texture), an unpredictable and often "poor" organoleptic quality remains a major complaint in customers (Stanley *et al*., 2014). To address this challenge, some breeding programs started to include eating quality traits (such as taste and aroma) as major targets of selection (Bassi and Foschi, 2020). Sugars (generally approximated as soluble-solid content, SSC), acids (mainly determined by organic acid content, OA) and their balance (i.e. sugar/acid ratio or *BrimA* index) largely contribute to apricot fruit taste, both affecting the sweetness perception and the overall degree of liking (Bartolozzi *et al*., 1997; Stanley *et al*., 2013; Fan *et al*., 2017). The close relation between sweetness and consumers' acceptability has been previously investigated in peach (Delgado *et al*., 2013; Echeverría *et al*., 2015) and apricot (Fan *et al*., 2017), although relying on a relative low number of accessions.

Other than a crucial ripening index for establishing the proper harvest time, sugars and acids content are important criteria for apricot characterization (Bassi and Selli, 1990; Bassi and Negri, 1991; Souty *et al*., 1991). Compared to peach, apricot has not been clearly differentiated for acids content (e.g., acid and low-acid types), either based on the fruit juice pH or titratable acidity (TA). A tendency toward the reduction of TA has been also observed in many recently released apricot cultivars (Tricon *et al*., 2010) and in most important Turkish accessions meant for drying (such as 'Hacıhaliloğlu' and 'Kabaaşı') (Karabulut *et al*., 2018).

In stone fruits, acidity mainly depends on OAs content, in turn determined by the balance of their biosynthesis, catabolism, transport, accumulation and storage into vacuoles through the activity of specific proton pumps (Ruffner *et al*., 1984; Walker and Famiani, 2018). At plant level, OAs ensure redox equilibrium generating ionic gradients across membranes and supply substrates for other related metabolic pathways. Sourness perception is not only related to total acids concentration but also to their qualitative composition, due to different sensorial impact of each acid on taste appreciation.

Nevertheless, many biochemical and physiological aspects of OAs metabolism have been scarcely investigated in apricot. In peach, malic acid is mostly synthetized in the cytosol by phosphoenolpyruvate carboxylase (PEPC) and NAD-dependent malate dehydrogenase (MDH), while citric acid derives from tricarboxylic acid cycle (TCA) through mitochondrial citrate synthase activity (Etienne *et al*., 2002; Borsani *et al*., 2009). Interestingly, apricot shows three copies of citrate synthase gene compared to the two in other *Prunus* species such as peach and almond (Jiang et al., 2019). TA and OAs concentrations decrease from the early stages of fruit growth to the full-ripen stage, being used as respiratory substrates (Etienne *et al*., 2002; Xi *et al*., 2016). In apricot, OA content occurred as a continuous distribution in diverse progenies, where the acids patterns seemed highly dependent on each genotype and relatively constant over years -regardless of the variability in absolute values- (Guichard and Souty, 1988; Bassi *et al*., 1996; Ruiz *et al*., 2010). Malate, citrate and quinate have been described as the most abundant OAs in apricot flesh and skin, accounting for more than 95 % of the total OA content at fruit maturity stage (Bassi *et al*., 1996; Gurrieri et al., 2001; Schmitzer *et al*., 2011; Fan *et al*., 2017). Differences in content and profiles of OAs between flesh and skin were also observed during ripening (Xi *et al*., 2016). In particular, the malate-citrate ratio appeared extremely variable in apricot, ranging from 0.2 to 8.8 (Gurrieri *et al*., 2001). Some accessions showed the ability to selectively accumulate malic or citric acid in mesocarp cells (Bassi and Selli, 1990).

This work investigates fruit acidity and OAs patterns in flesh and skin within an apricot germplasm collection of 164 accessions. The aim was enriching the knowledge on the variability of OAs contents and patterns in apricot over two years and describing the distribution of other fruit quality-related parameters to extend the availability of plant material used by breeders.

MATERIALS AND METHODS

Plant material and experimental design

The collection of apricot accessions was maintained at 'Centro Ricerche Produzioni Vegetali' (*CRPV*, www.crpv.it) located near Imola (North-East Italy). Apricot trees were grown on *Mirabolan 29C* rootstock. Ten uniform apricot fruits were randomly picked at full maturity stage ("ready-to-eat", MD) from 94 and 128 accessions (2 to 4 replicated trees per accession) in seasons 2017 and 2018, respectively. A total of 164 unique accessions from the apricot collection were analyzed (**Supplementary Table 1**), with 58 accessions recorded in both years.

Analyses of apricot fruit-quality parameters

Full ripening degree (estimated as the index of absorbance difference, I_{AD}) was expressed as the average value read for each fruit cheeks by a DA-meter portable spectrometer (Sintéleia S.r.l., Bologna, Italy). Individual fruit fresh weight (FW) was determined in grams (g) using a precision scale. Firmness was measured by a constant rate digital penetrometer (Andilog Centor AC TEXT08) test after removing a round area (1.5 cm of size) of apricot skin from the middle of both fruit cheeks by a slicer. The penetrometer was equipped with a flat metal plunger (6 mm) and motorized by a basic test stand (BATDRIVE) set at 5 mm s^{-1} of speed. Firmness was expressed in Newton (N). Dry matter (DM%) was estimated as the ratio of the weight (g) before and after oven-drying the samples at 60° C for 72 hours. Soluble solids content (SSC) was measured using a digital refractometer after the samples' centrifugation at 5000 rpm for 20 minutes at 4°C in order to clarify the flesh juices removing the heavier particles. SSC values were expressed as °Brix. TA determination was carried out preparing three biological replicates of flesh juices and three of skin juices. Four grams of apricot skin for each replicate were removed from the flesh, diluted 1:10 (w v^{-1}) in bi-distilled water and then mixed by an immersion blender. Fruit flesh replicates (50 mL each) were prepared using a juicer after complete apricot skin removal. Skin juices were prepared blending 4 g of skin with 1:10 (w v^{-1}) bi-distilled water. After centrifugation at 5000 rpm for 20 minutes at 4°C, 5 mL of clarified flesh and skin juices were diluted up to 50 mL with ultrapure water (18.2 MΩ cm^{-1} at 25°C). TA measurements were performed using an auto-titrator instrument (CRISON, Crison Instrument, Spain). Acidity was determined by successive addition of 0.1 N NaOH (Merck, KGaA, Germany) up to pH 8.30 and was expressed as g L^{-1} of malic acid.

Determination of organic acids qualitative and quantitative profiles

Ten OAs (cis-aconitate, citrate, fumarate, galacturonate, malate, oxalate, quinate, shikimate, succinate and tartrate) were detected by high-pressure liquid chromatography (HPLC) technique. For each run lasting 30 min, OAs determination was performed reading juice samples with the detector set at 210 nm. Calibration curves were built injecting sequential dilutions of OAs standards stock solutions (Fluka-Sigma-Aldrich; St. Louis, MO, USA) into the column. The retention time (*tr*, **Supplementary Figure 1)** was determined by injecting the standard alone and then mixed solutions at different OAs concentrations and compositions. The addition of internal standards into some juice samples further validated the presence of target OAs. To avoid interference between calcium ions and column resin, 100 µL of 0.5 % (w v^{-1}) Ethylenediaminetetraacetic acid (EDTA) were added to each mL of standard solutions and juices. Samples and standard solutions were filtered through a 0.45 µm nylon membrane (CHROMACOL, LTD, UK) before HPLC analysis.

A total of 2 mL of clarified supernatant were collected from each flesh and skin sample and transferred into an Eppendorf® tube to be further centrifuged at 14,000 rpm for 15 minutes at 4°C. Determination was performed injecting 5 µL of the samples into a Perkin Elmer LC200 series HPLC system equipped with a Jasko 975 UV/VIS detector (JASCO 28600, Mary's Court, Easton, MD) and an Aminex HPX-87 Ion Exclusion column (300 x 7.8 mm; Bio-Rad Laboratiories, Inc.). The analysis conditions were set at 65 °C (column temperature) with a flow rate of 0.6 mL min^{-1} and using 4 mM H_2SO_4 as elution solvent under isocratic elution. Data processing was carried out by *Chrom Workstation* 6.2 software where OAs peaks were identified by comparing relative retention times. Manual integration of each OAs peak avoided the over-estimation of the areas in each chromatogram. Areas quantification and conversion into concentrations (ng μL^{-1}) relied on the calibration curves previously built. Furthermore, OAs profiles of some samples were validated qualitatively and quantitatively through the ultra-high-performance liquid chromatography–high-resolution mass spectrometry (UHPLC-HRMS) method. Tests performance used an Acquity UHPLC separation module (Waters, Milford, MA, USA) coupled with a model Exactive Orbitrap MS through a HESI-II probe for electrospray ionization (Thermo Scientific, USA) set in negative ion mode. OAs separation was carried out using -3.0 kV of spray voltage. Voltages of capillary, tube lens and skimmer were equal to -27 V, -80 V and -16 V, respectively. Flow-rate of gas sheath and of auxiliary gas was 55 (arbitrary units) and 15 (arbitrary units), respectively. Heater and capillary temperature were set at 120° C

and 320° C, respectively. OAs separation was carried out on a 1.8 µm HSS T3 column (150x2.1 mm, Waters) with a flow-rate of 0.45 mL min^{-1}. The eluents were 0.05% HCOOH in MilliQ-treated water (solvent A) and CH_3CN (solvent B). Five µL of each sample were separated by UHPLC using the following elution gradient: 0 % B for 5 min, 0-80 % B in 1 min, 80 % B for 3 min and then return to initial conditions in 1 min. Column and samples were kept at 40° C and 15° C, respectively. UHPLC eluate was investigated in full scan MS in the range (m z^{-1}) of 50-1000 u. The resolution, AGC target, maximum ion injection time and mass tolerance were 50 K, 1E6, 100 ms and 2 ppm, respectively. Formic acid dimer [2M-H]-, that had an ion with m z^{-1} 91.0038 u, represented the lock mass.

MS data were processed using *Xcalibur* software (Thermo Scientific).

Statistical data analyses

All descriptive statistical analyses (maximum and minimum values, mean, pooled standard deviation between the two harvest years and frequency distribution) were carried out by *RStudio* (version *1.3.1056*) in *R* environment (version *3.6.3*). Fruit quality-related attributes distributions were tested for normality by Shapiro-Wilks statistic. Among all the fruit parameters, only flesh TA values seemed to follow a normal distribution (*p-value* = 0.11), leading to calculate Spearman's correlation coefficients (ρ) in *corrplot* package (version 0.84). PCA analysis was performed by *RStat* and *factoextra* packages (version *1.0.7*) in *RStudio*. Singular values decomposition (SVD) of each principal component, followed by scaling and centering, allowed the explanation of the variance found in the analyzed apricot collection dataset.

RESULTS

Titratable acidity and organic acids profiles in flesh and skin

Based on fruit quality evaluations in both seasons, titratable acidity (TA) of flesh and skin was strongly correlated across years (correlation coefficient of 0.83 and 0.55, respectively; **Supplementary Table 2**) indicating a low seasonality-dependence. Flesh TA ranged between 3.69 g L^{-1} of malic acid in 'BO06603111' and 23.65 g L^{-1} in 'BO06628081', with an averaged value of 12.64 g L^{-1} in the whole panel. Skin TA varied from a minimum of 3.79 g L^{-1} of malic acid in 'BO06603111' to a maximum of 24.87 g L^{-1} in 'Zebra', with an averaged value of 13.78 g L^{-1} in the totality of accessions. Frequencies and distributions of TA values were calculated on 164 unique accessions (**Figure 1**). TA of fruit skin and flesh was similar in

most of the accessions, with a ratio averaging of 1.11 (**Supplementary Figure 2**). Some cases of low or high TA ratio (skin *vs.* flesh) were also observed, for instance 'BO92618086' (0.50) and 'Harval' (2.09).

Over two-seasons, the ten OAs in flesh and skin (**Supplementary Table 3** and **Supplementary Table 4**) showed a reduced within-year variability among the biological replicates of each accession. Across-years correlation was stronger for the most abundant OAs and weaker for the others, ranging between 0.31 – 0.89 in flesh and 0.25 – 0.89 in skin (**Supplementary Table 5** and **Supplementary Table 6**). Among all the target OAs in flesh, malate (MAL) and citrate (CIT) were the most abundant and representative in all accessions, ranging from minimum values such as 1.68 g L^{-1} in 'Gilgat' and 0.50 g L^{-1} in 'BO04602023' to maximum values as 24.49 g L^{-1} in 'Bora' and 17.09 g L^{-1} in 'BO06628081' (**Supplementary Figure 3**). MAL and CIT in skin varied from 0.86 g L^{-1} (in 'Mono') and 1.57 g L^{-1} (in 'Royal Roussilon') to 29.11 (in 'Bora') and 29.19 g L^{-1} (in 'BO04639027'). Frequencies and distribution of MAL (**Figure 2**) and CIT (**Figure 3**) were highly variable across the panel, although average contents for both OAs were similar between flesh and skin with a value close to 6 g L^{-1}. MAL and/or CIT accumulation showed to be strongly genotype-dependent. Large MAL content was associated to low CIT content (and *viceversa*), both in flesh and skin (**Supplementary Figure 4**). Notable differences were found in 'BO06613160' flesh (MAL/CIT ratio of 17.33) and in 'BO06613160' skin (MAL/CIT ratio of 15.91). MAL/CIT ratio was similar and highly correlated (**Supplementary Table 5** e **Table 6**) in most flesh and skin of the same accession, suggesting only slight seasonal effects. Succinic acid (SUC) was the third most abundant OA, reaching values of 2.56 g L^{-1} in 'Yamagata' flesh and 3.27 g L^{-1} in 'BO04639027' skin (**Figure 4F** and **5F**). SUC was always detected in flesh, except in five accessions ('BO03605044', 'BO03614033', 'BO04639261', 'Harostar' and 'Pellechiella'). Regarding other OAs, their content was less abundant, varying in relation to the genotype and not always in detectable amount (**Figure 4**, **Figure 5**, **Supplementary Table 3** and **Supplementary Table 4**). Interestingly, tartrate (TRT) was largely observed in skin rather than flesh (maximum content of 2.09 in 'Royal Roussillon' *vs.* 0.07 g L^{-1} in 'BO04639405'). Also, galacturonate (GAL) was more abundant in skin with a maximum of 1.25 g L^{-1} in 'Bergecot'. On the contrary, quinate (QUI) content was very similar between flesh and skin, with maximum concentrations of 2.05 and 1.59 g L^{-1}, respectively. Shikimate (SHI) and cis-aconitate (CIS) were less frequently detected in flesh and skin and mostly in trace amounts. Oxalate (OX) was almost undetected in the analyzed apricots while fumarate (FUM) was always present, however in

traces, ranging between 0.003 – 0.058 in flesh (**Supplementary Table 3**) and 0.001 – 0.030 g L^{-1} in skin (**Supplementary Table 4**).

Correlation among fruit-quality attributes in flesh and skin

Correlations among TA, OAs and other fruit-quality attributes (i.e. MD, SSC, FW, DM% and I_{AD}) flesh and skin were tested (**Figure 6**). Almost all OAs and fruit parameters showed a relatively high across the two harvesting seasons (**Supplementary Table 2, 5** and **6**), allowing to average the replicated measurements. Significant correlations were found among many fruit-quality attributes: TA was strongly correlated between flesh and skin ($\rho = 0.72$) and positively linked to the total OA content (with coefficients of 0.86 and 0.83, respectively). The content of almost all OAs (except for OX and CIS) in skin was related to the corresponding ones in flesh, with correlation coefficients ranging up to 0.81. Although both CIT and MAL were significantly more abundant than the other OAs, CIT seemed to largely correlate with the overall TA (ρ of about 0.50). Total OAs content in flesh and skin was increased by the presence of CIT ($\rho = 0.47$ and 0.61, respectively), MAL (0.43 and 0.44) and SUC (0.22 and 0.21) and negatively affected by TRT (-0.25 and -0.14). TRT content was correlated to FUM in flesh (0.58) and SHI in skin (0.32). In both skin and flesh, SUC content was positively related to CIS concentration (0.41 and 0.60). In flesh, MAL was negatively affected by CIT and FUM (–0.49 and –0.39) while QUI content seemed to be affected by both SHI and TRT. Other interesting correlations were found between SSC and DM%, both negatively correlated to TA and positively to MD.

PCA analysis

Principal component analysis (PCA) was performed on TA, flesh and skin OAs content and the other quality traits to discriminate the most relevant attributes. The first two components (*PC1* and *PC2*) accounted for 30.5% of total variability (**Figure 7**). *PC1* was positively and strongly associated to TA of flesh and skin, but negatively associated to MD, SSC, DM% and FUM. *PC2* was positively influenced by MAL and MAL/CIT ratio (MAL/CIT), although negatively affected by CIT. 'BO05634124' and 'Tsunami' showed a major contribution on flesh and skin TA, 'Bora' on MAL, 'Tondina di Costigliole' and 'BO92639043' on CIT and 'BO92618086' on FUM. Late ripening accessions such as 'BO04639405', 'Autumn Royal', 'BO04639261' and 'Augusta 2' showed strong correlation of SSC and DM% with MD.

DISCUSSION

The present work pointed out a considerable diversity among accessions in the analyzed apricot germplasm collection, probably related to self-incompatibility and long domestication history of apricot species (Faust *et al*., 1998). Similar findings were achieved by previous studies focused on taste-related compounds (Audergon *et al*., 1991*a*; Audergon *et al*., 1991*b*; Bassi *et al*., 1996; Gurrieri *et al*., 2001; Chen *et al*., 2006; Ruiz and Egea, 2008; Bureau *et al*., 2009; Fan *et al*., 2017). This wide variability could provide valuable information for renewing the commercial cultivars array cultivated worldwide, introducing new phenotypes with superior organoleptic quality attributes. Both TA and OAs profiles seemed more dependent on genotype rather than seasonal effects, as confirmed by a previous work (Bassi *et al*., 1996).

A major genetic contribution to phenotypic variance for TA, citric and malic acids contents was recently observed in a segregating progeny, although with a significant year and genotype-by-year interaction effects ascribed to seasonal variation in temperature regimes (Nsibi *et al*., 2020). In contrast, the effect of fruit maturity degree at harvest on acid-related traits was almost negligible (Nsibi *et al*., 2020). Interestingly, SSC and TA were negatively correlated (ρ= -0.42), a trend already recorded in apricot (Xi *et al*., 2016; Gurrieri *et al*., 2001) and likely linked to the conversion of OAs into substrates for other metabolic pathways.

In the analyzed apricot collection, biosynthesis and accumulation of OAs as well as TA levels seemed dependent on maturity date, both in flesh and skin, as supported by the negative correlation between traits. Early-ripening apricot accessions showed higher fumarate, tartrate and cis-aconitate amounts in flesh, while shikimate and fumarate in skin. On the other hand, late-ripening accessions showed higher content of succinate, malate, quinate and oxalate. Whether the MD effects on acidity-related traits is dependent on developmental and/or environmental (i.e. temperature-mediated TCA metabolism) factors should deserve further investigations in order to disentangle non-genetic effects on these attributes, and improve the selection process in future apricot progenies.

TA widely ranged from lesser than 4 to more than 24 g L^{-1}, with similar values between flesh and skin in most of the accessions. Similar to TA, OAs profiles remained almost stable within each accession. Most important, consistency of OAs patterns between flesh and skin was observed also in case of variations in their absolute concentrations. Total OAs content highly correlated to overall TA in flesh and skin (0.89

and 0.91, respectively), suggesting a possible two-way pattern expression of acidity-related compound accumulation.

Similar to peach (Moing and Svanella 1998; Etienne *et al*., 2013; Nowicka *et al.*, 2019; Baccichet *et al*., 2021; Zheng *et al*., 2021), malate and citrate were the most abundant OAs with concentrations up to 29 g L^{-1} in skin of some accessions. A predominant accumulation of malate or citrate was observed in each accession, as reported in other studies but without analyzing such a large number of accessions (Souty *et al.*, 1991; Gurrieri *et al*., 2001; Karabulut *et al*., 2018). This evidence should be more explored in the future to characterize a different behaviour in metabolic or catabolic processes during fruit ripening and post-harvest stages. MAL/CIT ratio remained highly stable between fruit flesh and skin but showed a remarkable variation across accessions. As previously reported (Souty *et al*., 1976; Gurrieri *et al*., 2001), this index is a useful chemical parameter for cultivar classification and an important quality attribute for their characterization. Malate has a different taste compared to citrate, less sour and stronger in mouth (Colaric *et al*., 2005; Xi *et al*., 2016), and in apricot the acidity perception is best correlated to malate than to citrate (Bureau *et al*., 2006). Thus, the effect of different MAL/CIT ratio on sensory perception is a topic that should merit further evaluations by a trained panel to determine the specific perception of the individual acid and, in turn, the final destination each accession, either fresh or processed.

Out of the ten OAs considered in this work, quinate, shikimate and tartrate do not belong to the TCA cycle. Quinate content was more stable in flesh across years and was reported at low concentration in other species, such as peach (Moing and Svanella, 1998; Etienne *et al*., 2013). Shikimate is generated from pentose phosphate or phosphoenolpyruvate (PEP) pathways and is a precursor of aminoacids (such as Tyrosine) and secondary metabolites (such as flavonoids and phenylpropanoids) often characterized in apricot (Weaver and Herrmann, 1997; Ruiz *et al*., 2005; Bureau *et al*., 2009; Maeda and Dudareva, 2012; Campbell *et al*., 2013; Cheynier *et al*., 2013; Le Bourvellec *et al*., 2018; Huang *et al*., 2019; Gómez-Martínez *et al*., 2021). Polyphenols are responsible for fruit astringency (i.e. phenolic acids such as chlorogenic acid and neochlorogenic acid) and pigments (e.g., anthocyanins such as cyanidin-3-O-rutinoside, cyanidin-3-O-glucoside and peonidin-3-O-rutinoside) and they seem to have antioxidant benefits to human diet (Bureau *et al.*, 2009; Ruiz *et al.*, 2005; Tanaka *et al*., 2008; Campbell *et al*., 2013; Jin *et al*., 2016; Luo *et al*., 2016). As a consequence, insights into a possible relationship between shikimate and polyphenolic compounds content

might be undertaken. Indeed, breeding apricot for skin and flesh features may impact the organoleptic and nutritional properties, influencing the final fruit quality and market's success.

Tartrate characterizes OAs profiles of other species as grapevine and with oxalate and L-threonate seems to be a catabolic product of ascorbate (Vitamin C) in plants (DeBolt *et al*., 2007). Tartrate did not show a correlation with oxalate content and it was mostly present at low concentrations in the whole apricot panel, a consistent finding to a previous work (Xi *et al*., 2016). Interestingly, tartrate content was much higher in skin rather than in flesh, allowing to assume a tissue-specific accumulation for this OA in apricot. A role in defence against pathogens or in protection of the fruit from direct sun-exposure could explain a different distribution of tartrate between skin and flesh, which should be taken into account since fresh and dried apricots are consumed with skin.

Galacturonic acid is the most important constituent of pectins, polysaccharides concurring in building the plant cell walls. Fruit ripening is characterized by pectins depolymerisation and generally leads to flesh softening and decreased fruit firmness (Femenia *et al*., 1998; Brummel, 2006; Goulao and Oliveira, 2008; Kovács *et al*., 2008). However, no evident relation was found between galacturonate and firmness, probably due to harvesting done at full physiological ripening stage.

CONCLUSIONS

A large apricot collection germplasm was explored for several fruit-quality related attributes, showing a huge variability particularly for titratable acidity and organic acids content. The screening of flesh and skin tissues has revealed an accession-dependent organic acids patterns, in particular for malate and citrate, resulting negatively correlated. Another interesting evidence concerns the relationships between maturity date and soluble solids content, which open to a fruit quality oriented selection and looking forward genomic association studies for these traits. Still, the results seem promising and may provide advantageous information for the next breeding generations. Additional studies will be needed to clarify the metabolic pathways involved, the accumulation route of each organic acid and the role of genetic variation in shaping the differences observed across germplasms. Also, the impact and contribution of specific organic acid on taste should be further explored, to support the selection of next generations apricot cultivars.

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CONFLICT OF INTEREST

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

AUTHORSHIP

IB: collected and analysed the data, performed phenotypic analyses and drafted the manuscript; *CR*, helped in data collection and performed phenotypic analyses; *SA*, developed and improved the adopted method in performing HPLC analyses; *GC*, helped in phenotypic analysis; *BD* and *MC* conceived the original idea and supervised the project. *IB*, *CR*, *BD* and *MC* critically revised the manuscript.

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FIGURE CAPTIONS

Figure 1. Frequency (A and B) and distribution (C) of TA values of skin and flesh in apricot germplasm collection. The two histograms report the frequency of acidity content (as g L^{-1} of malic acid) recorded for fruit skin (A) and flesh (B), separately, in the assessed apricots (164 unique accessions). Two-years measurements for 58 common accessions were averaged.

Figure 2. Frequency (A and B) and distribution (C) of malic acid content (g L^{-1}) in apricots skin and flesh. The two histograms represent the malic acid content frequency (g L^{-1}) observed in fruit skin (A) and flesh (B) in the analysed apricot collection (164 unique accessions). Two-years measurements for 58 common accessions were averaged. In skin (C), the lowest amount was observed in 'Mono' (0.87 g L^{-1}) and the largest in 'Bora' (29.12 g L^{-1}). In flesh (C), the minimum value of 1.68 g L^{-1} was observed in 'Gilgat' and the maximum one of 24.49 g L^{-1} in 'Bora'.

Figure 3. Frequency (A and B) and distribution (C) of citric acid content (g L^{-1}) in apricot fruit skin and flesh. The two histograms represent the citric acid content frequency (g L^{-1}) observed in fruit skin (A) and flesh (B) in the analysed apricot collection (164 unique accessions). Replicated measurements for 58 common accessions were averaged. The minimum content was observed in 'BO04602023' flesh (0.51 g L^{-1}) and in 'Royal Roussilon' skin (0.16 g L^{-1}) (C). On the contrary, the maximum value was found in 'BO06628081' flesh (17.09 g L^{-1}) and in 'BO04639027' skin (29.19 g L^{-1}) (C).

Figure 4. Quantitative profiles (ng μL^{-1}) of less abundant OAs detected in apricot flesh (164 unique accessions). Succinic acid (F) was the third most abundant OA in flesh, followed by quinic acid (E), shikimic acid (G), oxalic acid (A) and tartaric acid (C). Cis-aconitic acid (B) and fumaric acid (H) were detected in trace amounts. 'BO92618086', 'Congat', 'Harlayne' and 'Royal Roussilon' were removed from histograms of shikimate, oxalate, cis-aconitate and tartrate because out of the mean range of OAs concentrations.

Figure 5. Quantitative profiles (ng μL^{-1}) of minor OAs detected in apricot skin (164 unique accessions). Succinic acid (F) was highly abundant in apricot skin followed by quinic acid (E), galacturonic acid (D) and cis-aconitic acid (B) and tartaric acid (C) reached relevant concentrations in skin. Shikimic acid (G) and fumaric acid (H) were detected in all accessions but without reaching a large content. 'BO04639027', 'Royal Roussilon', 'BO92618086' and 'Trivini' were respectively removed from histograms of succinate, tartrate, shikimate and cis-aconitate because out of the mean range. Similarly, 'BO04614003', 'Mirlo Naranja', 'Reale Baldassarri', 'Murciana', 'Portici' and 'GG 98-71' were not reported in oxalate histogram.

Figure 6. Correlation test among fruit quality traits and OAs profiles recorded in apricots flesh and skin, separately, during the two harvest seasons. A total of 164 unique apricot accessions were considered and replicated measurements for each accession were averaged. Correlations were significant * at the 5%, ** 1% and *** 0.1% level. OAs are reported in different colours for flesh and skin. *MD*, maturity date (as Julian Days); *TA*, titratable acidity (g L^{-1} of malic acid) for flesh and skin, separately; *SSC*, soluble solids content (°Brix); *DM%*, dry matter percentage**;** *FW*, fresh weight (g); I_{AD}, chlorophyll absorbance index; *F*, firmness; *OAs*, total sum of organic acid content in flesh and skin, separately; *CIS*, cis-aconitate; *CIT*, citrate; *FUM*, fumarate; *GAL*, galacturonate; *MAL*, malate; *OX*, oxalate; *QUI*, quinate; *SHI*, shikimate; SUC, succinate; *TRT*, tartrate.

Figure 7. PCA plot on fruit quality attributes. The analysed variables are coloured differently for flesh (in green), skin (in orange) and the other fruit quality attributes (*FQ*, in violet). *DM%*, dry matter in percentage**;** *F*, firmness (expressed in Newton); *FW*, fresh weight (g); *MD*, maturity date (as Julian Days); *IAD*, chlorophyll absorbance index; *SSC*, soluble solids content (°Brix); *TA*, titratable acidity (g L^{-1} of malic acid); *CIS*, cis-aconitate; *CIT*, citrate; *FUM*, fumarate; *GAL*, galacturonate; *MAL*, malate; *OX*, oxalate; *QUI*, quinate; *SHI*, shikimate; SUC, succinate; *TRT*, tartrate; *MAL/CIT*, malate/citrate content ratio.

SUPPLEMENTARY FIGURE AND TABLE CAPTIONS

Supplementary Figure 1. Chromatograms and retention time of organic acids patterns in 'Lito' flesh (A) and skin (B) and in 'Zebra' flesh (C) and skin (D). The peaks reported are: *MP*, mobile phase; *1*, oxalic acid (not present in all these accessions); *2*, cis-aconitic acid; *3*, citric acid; *4*, tartaric acid; *5*, galacturonic acid; *6*, malic acid; *7*, quinic acid; *8*, succinic acid; *9*, shikimic acid and *10*, fumaric acid.

Supplementary Figure 2. TA ratio between fruit skin and flesh. The largest amount of individuals had similar TA values between flesh and skin. The minimum (0.50) and maximum (2.09) records were relative to 'BO92618086' and 'Harval', respectively.

Supplementary Figure 3. 'Bora' and 'BO06628081' accessions compared to the corresponding maximum content of malate (A) and citrate (B) in the whole collection. Malate and citrate were the most abundant OAs observed in the apricot panel, reaching the largest concentration in 'Bora' flesh (24.49 g L^{-1}) and skin (29.11 g L^{-1}) and in 'BO06628081' flesh (17.09 g L^{-1}), respectively.

Supplementary Figure 4. Malate/citrate (MAL/CIT) content ratio in apricots skin (A) and flesh (B). Most of the accessions showed a MAL/CIT ratio between 0.12 and 1.25. A total of three accessions for fruit flesh ('BO04610060', 'Bora' and 'BO04602023') and six for fruit skin ('BO04602023','BO99601019', 'Aurora', 'BO04610060', 'Bora' and 'Royal Roussilon') had values greatly out of mean range and were not included in these histograms.

Supplementary Table 1. List of apricot accessions in the analyzed panel.

Supplementary Table 2. Spearman's test correlation matrix among some fruit quality attributes recorded across the two harvesting seasons 2017 and 2018. The correlation coefficients are significant when *p-value* < 0.05, 0.01 or 0.001 (respectively * significant at the 5% level, ** significant at the 1% level, *** significant at the 0.1% level). *TA,* titratable acidity (expressed as g L^{-1} of malic acid) measured separately for flesh and skin; *FW*, fresh weight (g); *MD*, maturity date (calculated as Julian days); *IAD*,

chlorophyll absorbance index; *DM%*, dry matter percentage; *F*, firmness (in Newton); *SSC*, soluble solids content (°Brix).

Supplementary Table 3. Quantitative profiles (g L^{-1}) of ten OAs detected in the flesh of the apricot collection through the HPLC analysis. OAs concentrations in replicated apricot accessions were averaged across years. Minimum, maximum, mean values and pooled standard deviation (SD_{Pooled}) were estimated for each OA found in fruit flesh.

Supplementary Table 4. Quantitative profiles (g L^{-1}) of ten OAs detected in the skin of the apricot collection via HPLC analysis. OAs concentrations in replicated apricot accessions were averaged across years. Minimum, maximum, mean values and pooled standard deviation (SD_{Pooled}) were estimated for each OA found in fruit skin.

Supplementary Table 5. Spearman's test correlation matrix among OA content in apricots flesh recorded across the two harvesting seasons 2017 and 2018. The correlation coefficients are significant when *p-value* < 0.05 (* significant at the 5% level, ** significant at the 1% level, *** significant at the 0.1% level). *OX*, oxalate; *CIS*, cis-aconitate; *CIT*, citrate, *TRT*, tartrate; *GAL*, galacturonate; *MAL*, malate; *QUI*, quinate; *SUC*, succinate; *SHI*, shikimate; *FUM*, fumarate. *MAL/CIT*, malate/citrate content ratio.

Supplementary Table 6. Spearman's test correlation matrix among OAs content in apricots skin recorded across the two harvesting seasons 2017 and 2018. The correlation coefficients are significant when *p-value* < 0.05 (* significant at the 5% level, ** significant at the 1% level, *** significant at the 0.1% level). *OX*, oxalate; *CIS*, cis-aconitate; *CIT*, citrate, *TRT*, tartrate; *GAL*, galacturonate; *MAL*, malate; *QUI*, quinate; *SUC*, succinate; *SHI*, shikimate; *FUM*, fumarate. *MAL/CIT*, malate/citrate content ratio.