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Research Paper

Chemometric classification of early-ripening apricot (*Prunus armeniaca*, L.) germplasm based on quality traits, biochemical profiling and in vitro biological activity

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ABSTRACT

In the present study, eight early-ripening apricot cultivars of the Italian and international germplasm were evaluated during three years of investigation (2013–2015), according to their quality traits, biochemical composition, antiradical capacity and hydroxycinnamic acid (HCA) profile, using a chemometric approach. Among cultivars analysed, the highest fresh weight was detected in 'Maia' (106 ± 3 g), whereas the lightest fruits were produced by 'Ottavianese' cv (51 ± 4 g). 'Orange Rubis' and 'Maia' were characterized by the highest levels of dry matter, which represent a key processing parameter for the production of dried apricots. The highest content of bioactive compounds such as total phenols and flavans were found in 'Spring Blush', Orange Rubis' and 'Monaco Bello', indicating a greater susceptibility to browning during processing. Chlorogenic acid was the most abundant hydroxycinnamic acid found in all tested genotypes, being 'Portici' the richest one (338 ± 21 μg g^{-1} on dry basis). High significant correlations were found among parameters analysed, especially between colour coordinates and bioactive compounds. Finally, application of stepwise discriminant analysis to apricot samples showed that total phenols, total flavans and antiradical capacity were the most important variables to differentiate the cultivars analysed. Besides, principal component analysis made it possible to establish similarities among the cultivars depending on their quality and biochemical characteristics. It is concluded that the combination of quality, biochemical traits analysis and chemometric techniques can be used as a consistent procedure to provide breeders with useful information about the identification and characterization of the most promising early ripening genotypes, both for fresh consumption and processing.

1. Introduction

Apricots are cultivated worldwide. Currently, Italy is the fifth world's producer of apricots for fresh consumption (FAOSTAT, 2014), while, in Europe, it is the largest producer, concentrating its production mainly in Campania, and Emilia-Romagna (Glisic et al., 2014). The demand from the market to develop and introduce new varieties with different characteristics, which made it possible to expand cultivation areas, production calendars, and improve technology with regards to production and post-harvest handling of these delicate fruits is increasing. However, breeders traditionally select new varieties mainly for external fruit traits (i.e., size and appearance) and/or improved pest resistance, with organoleptic and nutritional characteristics being a secondary goal. In spite of this, fruit quality is fundamental for the acceptance of different cultivars by consumers, due to the high competition in the markets with the presence of numerous new varieties, other fruits and other foods (European Commission, 2001; Iglesias and Echeverría, 2009). Abbott (1999) indicates that food quality, both fruit and vegetable one, is a concept, which includes sensory, mechanical and functional properties as well as chemical composition and nutritional values. The latter is a key point as fruit has long been promoted for its health benefits in preventing various cancer and age-related

Abbreviations: AC, antiradical capacity; BHT, butylated hydroxytoluene; CAE, catechin equivalents; CGA, chlorogenic acid; EC, commission regulation; DA, discriminant analysis; db, dry basis; DM, dry matter; EU, European Union; F, firmness; FLC, flavan-3-ols; GAE, gallic acid equivalents; HCAs, hydroxycinnamic acids; HPLC, high performance liquid chromatography; EC_{50}, mg of apricot on dry basis required to obtain 50% of scavenging; DAD, photodiode array detector; PCs, principal components; PCA, principal component analysis; SE, standard error; MANOVA, multivariate analysis of variance; DA, discriminant analysis; TA, titratable acidity; TCC, total carotenoid content; TSS, total soluble solids; TPC, total polyphenol content; DPPH·, 2,2-diphenyl-1-picrylhydrazyl radical;; W, fresh weight 2,2′; ABTS, -azinobis-(3-ethylbenzothiazolin-6-sulfonic acid); BHT, butylated hydroxytoluene

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diseases (Bazzano et al., 2002; Liu, 2003; Casacchia and Sofo, 2013). This is due to the presence of high-added-value bioactive compounds, named phytochemicals (Iriti and Faoro, 2006). These compounds possess strong antioxidant properties that enable them to scavenge free radicals, donate hydrogen, chelate metals, break radical chain reactions, and quench singlet oxygen in vitro and in vivo (Dai and Mumper, 2010). All these properties enable the fruits to act in the prevention of oxidative-stress-related diseases (Pandey and Rizvi, 2009). Among phytochemicals, the most abundant classes present in apricots are polyphenols and carotenoids (Erdogan-Orhan and Kartal, 2011). Among them, chlorogenic acid, catechin, rutin and β-carotene are the most abundant phytochemicals found in apricot varieties (Ruiz et al., 2005; Melgarejo et al., 2014). Particularly, chlorogenic acid (3-O-caffeoylquinic acid; named CGA) is the dominant phenolic compound in apricots (Dragovic-Uzelac et al., 2005, 2007). It is one of the secondary metabolites in plant species, whose beneficial role for human health is supported by a series of epidemiological, biological and biochemical data (Xiang and Ning, 2008). Several factors are reported to affect the content of these compounds in apricot fruits, and the genotype is the most important (Engel et al., 2010). Several authors reported that early ripening apricot varieties are characterized by a higher acidity and a lower total phenolic content compared to the other varieties that ripening later (Engel et al., 2010; Lo Bianco et al., 2010). Furthermore, Leccese et al. (2012) speculated that early ripening genotypes tend to have a lower total soluble solids:total acidity (TSS:TA) ratio than late ripening ones. This is a key point as TSS:TA is considered an indicator of taste quality (Caliskan et al., 2012) as consumer's preference for apricots is mainly determined by its sugar and organic acid content. In spite of these evidences, early season apricots represent an important potential for the market of apricots for fresh consumption, which could be enhanced through breeding programs aimed at improving the fruity attractiveness, making them more attractive to the consumer. In fact, apricot breeding supplies every year a fairly good number of improved varieties to meet different market needs, especially with the aim of expanding the production calendar. Nevertheless, there are some critical issues not yet fully addressed through breeding such as the increasing competition between apricots and a broad range of other fruits, as well as the consumer eating habits, which are changed in the last years, with a growing emphasis on sensory, nutritional and healthy properties of food. To meet these challenges, it is necessary to explore new germplasm for the production of new cultivars with improved sensory, qualitative and nutritional characteristics as well as to provide fruits to the market for long periods of time. However, to the best of our knowledge only a limited number of early- ripening apricot varieties has been fully characterized (Leccese et al., 2012). Starting from these considerations, the present research aimed to assess the influence of genotype on the overall quality traits and nutraceutical potential of eight early-ripening apricot cultivars, from Italian and international germplasm, with the aim to provide useful information to the breeders about the most promising genotypes with a potential impact for the market. To do this, quality and nutraceutical traits, hydroxycinnamic acid content and antiradical capacity of apricot fruits were studied. Moreover, a chemometric classification, using both discriminant analysis (DA) and principal component analysis (PCA) of genotypes analysed was performed based on fruit quality attributes, phytochemical profiles and antiradical potential, which allowed the discrimination of varieties based on different and similar properties, respectively. In addition, the present study describes for the first time the main qualitative and nutritional characteristics of two Italian early-ripening apricot varieties ('Maia' and 'Bora').

2. Material and methods

2.1. Chemicals

All used reagents were of analytical spectrophotometric grade (Carlo Erba, Rome, Italy). Folin-Ciocalteu reagent, gallic acid, catechin, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH·), 2,2′-azinobis-(3-ethylbenzothiazolin-6-sulfonic acid) (ABTS), potassium persulfate, and vanillin were purchased from Sigma-Aldrich (Milan, Italy). Chlorogenic acid used for identification and quantification purposes with HPLC was purchased from Sigma-Aldrich (Milan, Italy). Organic solvents used for chromatography were of HPLC ultra gradient grade (Sigma Aldrich, Milan, Italy), while the water employed was previously purified in a Milli-Q system (Millipore, Milan, Italy). 0.45-μm pore size membrane filters from Pall (Pall Corporation, Michigan, USA) were used for filtration of both mobile phases and samples.

Table 1
Geographical origin, ripening time and parental lines of early-ripening genotypes analysed.

Genotype	Code	Origin	Pedigree	Ripening time[a]
Procida	P	Italy	Sabelle × Ouardi	−22
Spring Blush®-EA 3126 TH	SB	France	Unknown	−16
Ischia	I	Italy	Sabelle × Ouardi	−16
Bora® – BO90610010	B	Italy	Early Blush × PA7005-2 (Rival × PA 63-265)	−11
Orange Rubis® – Coloumnie	OR	France	Unknown	−11
Ottavianese	O	Italy	Unknown	−11
Monaco Bello	MB	Italy	Unknown	−10
Maia – BO 99620131	M	Italy	Portici × Bora	−4

[a] Number of days before ripening of Goldrich (18 June).

2.2. Plant material and experimental design

Apricot fruits (*Prunus armeniaca,* L.) from eight very early- and early-ripening varieties (listed in Table 1) were collected in the experimental orchards of the Fruit Tree Research Centre of Rome (CREA-FRU, Italy), at commercial maturity stage on the basis of their skin ground colour (Ruiz and Egea, 2008).

All tested varieties were grafted on the same rootstock (Myrabolan 29C), spaced at 4.5 m × 2.5 m and conventional summer pruning, drip irrigation treatments and standard cultural practices were performed. For each variety, four plants were sampled, and fruits were collected from the outer layer of the canopy, avoiding the top, the bottom and the inner, shaded layer of the canopy. To minimise the environmental effects on all of the agronomic traits, data were collected across three consecutive years (2013–2015).

After harvest, the fruits were immediately transported to the laboratory and screened for uniformity, appearance and the absence of physical defects or decay. From harvested fruits, three replicate samples (15 fruits each) *per* each experimental tree and *per* each genotype were chosen at random, cleaned with MilliQ water, drained and gently blotted with a paper towel, then immediately analysed for the quality traits.

2.3. Fruit quality traits

Unpeeled apricots (90 fruits *per* genotype *per* year) were weighed, deprived of stones, homogenized, and the homogenate samples were analysed for total soluble solid (TSS) content using a digital refractometer (Refracto 30 PX, Mettler Toledo, Milan, Italy); data are given as °Brix. The method for the analysis of titratable acidity (TA) was based on titration of the acids present in the apricot juice with sodium hydroxide (0.1 N). Data are given as meq L^{-1}. The pH value was measured using a digital pH-meter (785 DMP, Methrom, Milan, Italy). Firmness was measured with a penetrometer (Fruit Pressure Tester FT011, TR snc, Forlì, Italy), using an 8 mm tip and expressed as kg cm^{-2}. Weight loss after drying fresh samples, until a constant weight