Phenolic, sugar and acid profiles and the antioxidant composition in the peel and pulp of peach fruits

Title header: Antioxidant profiles in the peel and pulp of peaches and nectarines

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Abstract

In this study, antioxidant compounds (ascorbic acid; total phenolic, flavonoid and anthocyanin contents; and relative antioxidant capacity) and the profiles of sugars, organic acids, polyphenols and mineral composition were compared in the peel and pulp tissues of nine commercial peach cultivars. The antioxidant compounds, measured by a 96-well-microplate-reader, showed differences among cultivars. The phenolic profile determined by UPLC resulted in the quantification of hydroxycinnamates, flavonols (only in peel), flavanols and anthocyanins, which were differently distributed in both tissues. Peels contained the highest phytochemical composition, with the exception of sugars and organic acids. We found that the contents of flavonoids, anthocyanins and total phenolic compounds measured by spectrophotometry and UPLC-MS methodologies were highly correlated. The Spanish cultivar Calanda Tardio showed the highest antioxidant and sorbitol contents. Venus had the highest contents of ascorbic and citric acids, and Big Top had the highest sucrose content.

Keywords: *Prunus persica*; nectarine-peach; antioxidant compounds; polyphenolic compounds; sugar and acid compositions; spectrophotometry; UPLC-MS; HPLC-DAD; Food analysis and food composition.

1. Introduction

Peach [*Prunus persica* (L.) Batsch] is an economically important crop in terms of world production (21.63 million tons in 2013) and surface area of cultivation (1.5 million ha; FAOSTAT 2016; <http://faostat3.fao.org/>). In Spain, peaches are the most important stone fruit crop, with Spain ranking third after China and Italy in world production (1.32 million tons in 2013) (FAOSTAT 2016; <http://faostat3.fao.org/>). Peach is also the most dynamic fruit species in terms of new cultivars released per year. In the last decade, new peach cultivars have originated from breeding programs in the USA, France and Spain (Byrne et al., 2012).

Peaches are a popular summer fruit, and there has been an increasing interest in their nutritional value (Wolfe et al., 2008). Many epidemiological studies suggest that increased consumption of stone fruit lowers the risk of chronic diseases, such as cardiovascular diseases, cancer and diabetes (Vinhaes et al., 2016). In particular, human consumption of peaches can prevent cellular oxidative stress caused by free radicals (Sun et al., 2002). Moreover, peach juice consumption has a protective effect against a combination of obesity-induced metabolic disorders, including hyperglycemia, insulin, leptin resistance and dyslipidemia (Noratto et al., 2015).

The beneficial effects of dietary intake of fruits are mainly due to the presence of vitamins (provitamin A carotenoids, and vitamin C), fibers, minerals (rich in potassium), and phytochemical compounds including, phenolic acids, flavonoids and anthocyanins (Manzoor et al., 2012b). Polyphenols are secondary metabolites with an important role in fruit quality because of their contribution to the taste, color and nutritional properties (Tomás-Barberán and Espin, 2001). Peach cultivars rich in polyphenols have higher antioxidant activities and are excellent sources of

phytochemical and natural antioxidants (Zhao, et al., 2015). Different phenolic compounds in peaches and nectarines have been characterized in both peel and flesh tissues, such as hydroxycinnamates, flavan-3-ols, anthocyanins and flavanols (Aubert et al., 2014; Simeone et al., 2012; Tomás-Barberán et al., 2001; Zhao, et al., 2015). Peel tissue contains large amounts of phenolics due to the presence of flavonols and high contents of anthocyanins (Scordino et al., 2012; Tomás-Barberán et al., 2001; Zhao, et al., 2015). The characterization of the phenolic profile in peach fruit could represent a useful tool for authenticity controls (Scordino et al., 2012).

Different methodologies have been used to determine phenolic compounds in peach fruit. Many authors have reported the quantification of antioxidant compounds as total phenolic, flavonoid, and anthocyanin contents and as relative antioxidant capacity by spectrophotometry UV-VIS methods (Abidi et al., 2011; Cantín et al., 2009; Font i Forcada et al., 2013). However, to avoid interfering substances and to identify individual polyphenols or to perform authenticity profiles in peach fruits, other methods, such as UPLC-MS and UPLC-DAD (Aubert et al., 2014) and HPLC-DAD-ESI/MS (Scordino et al., 2012; Tomás-Barberán et al., 2001), have been used.

Apart from their beneficial effects on health, peaches and nectarines are appreciated by consumers because of their sweetness, juiciness and flavor (Aubert et al., 2014). The edible quality of peaches and nectarines greatly depends on their total sugar and acid contents but also on individual sugar and acid composition, which has a significant impact on the perception of sweetness and sourness (Esti et al., 1997). Sucrose is the predominant sugar, and malic acid is the predominant organic acid, followed mainly by quinic and citric acids (Reig et al., 2013; Wu et al., 2003).

The main objective of this work was to evaluate the content of a series of metabolites associated with health and sensory quality in fruits of nine commercial peach cultivars. These metabolites were associated with the antioxidant properties (phenolic profile, ascorbic acid, total phenolic, flavonoid, anthocyanin contents, and relative antioxidant capacity) and flavor characteristics (sugars and acids composition). Two nectarines (Big Top and Venus) and seven non-melting flesh peach cultivars were included in the study. Peel and pulp were analyzed to estimate the relative contribution of both tissues to the nutritional and organoleptic value of these cultivars. The results found here may be of interest for a breeding program aimed to enhance nutritional value and, therefore, meet the expectations of consumers for fruit with high health benefits and a specific taste. As a complementary objective of this study, we compare the phenolic contents measured by spectrophotometry with those quantified by UPLC-DAD in both tissues.

2. Materials and methods

2.1. *Plant material*

Nine commercial varieties of peach and nectarines from the germplasm collection of the Experimental Station of Aula Dei-CSIC (Northern Spain Zaragoza) were included in this study (Table 1). Three trees per genotype were grown under standard conditions of irrigation, fertilization and pest and disease control, except for the Calante cultivar grown in Alcañiz (Teruel, Spain). All cultivars have round and yellow flesh fruits.

2.2. *Harvest and sample processing*

Twenty fruits per cultivar were handpicked at commercial maturity and assessed by peel fruit color (exhibited yellow-red color), flesh firmness and ease of detachment from the tree (Crisosto, 1994). Harvesting dates ranged from June (Crown Princess) to late

October 2015 (Calante Tardio and Calante), depending on the cultivar (Table 1). Physico-chemical parameters (fruit weight, firmness, soluble solids content (SSC), titratable acidity (TA), pH, and SSC/TA) were measured at harvest (Table S1.). Fruits were washed with deionized water and towel dried; the peel and pulp were separated using a sharp knife and were cut into small pieces. For further biochemical analysis, 5 g of peeled flesh fruit and 3 g of peel were weighted and immediately frozen in liquid nitrogen. Samples intended for the determination of antioxidant compounds, sugars and acids were stored at (-20°C) until analysis. Samples intended for the determination of ascorbic acid were kept in 5 ml of 5% metaphosphoric acid (HPO₃).

2.3. Extraction and biochemical determination

The ascorbic acid was extracted adding 5 ml of 5% HPO₃; total phenolics, flavonoids, polyphenols and antioxidant capacity (RAC) were extracted with 10 ml of a mixture of MeOH/H₂O/Formic acid (60:38:2 v/v/v); and sugars and acids were extracted with 10 ml of water. Frozen fruit samples were thawed on ice and homogenized with a polytron (T25D Turrax, IKA Works, Inc.; Wilmington, NC, USA); then, the pulp and peel samples were centrifuged for 20 min and 40 min, respectively, at 4°C and 30000 g (Avanti J-20XP, Beckman Coulter, Inc.; Brea, CA, USA). The final volume of supernatant was scored and used for the biochemical analysis. All chemicals were of analytical or HPLC grade when required and were purchased from Sigma-Aldrich (Saint Louis, MO, USA) and Panreac-Química (Barcelona, Spain). All reactions were adapted to measure antioxidant compounds (ascorbic acid, total phenolic, flavonoid and anthocyanin contents, and relative antioxidant capacity) using a 96-well microplate spectrophotometer (Biochrom Asys UVM 340, Microplate reader, Cambridge United

Kingdom). The standard calibration curves were prepared daily with eight points of concentration of the corresponding standard (Fig. S1).

The determination of ascorbic acid was based on the reduction of Fe (III) to Fe (II) by L-ascorbic acid followed by the formation of Fe (II) - 2, 2'-Bipyridil complex (Okamura, 1980). Fifty μ l of the extract was mixed in a microplate, with equal amounts of orthophosphoric acid, 2, 2'-Bipyridyl and FeCl_3 , to final concentrations of 11%, 0.8% and 0.3%, respectively; then, the plates were incubated at 37°C for 90 min. Absorbance was measured at 525 nm, and the results were expressed as mg of ascorbic acid (AsA) per 100 g of FW. Total phenolic content was determined according to the colorimetric method based on the chemical reduction of the Folin-Ciocalteu reagent (Singleton and Rossi, 1965). The method consisted of mixing 50 μ l of diluted extract in a microplate with 100 μ l of Folin-Ciocalteu's reagent (final concentration 0.1 N) and 50 μ l sodium carbonate (Na_2CO_3) (final concentration 3%), and the microplate was incubated at 23°C in darkness for one hour. Absorbance was measured at 765 nm, and the results were expressed in mg of gallic acid equivalents (GAE) per 100 g of FW. Total flavonoid content was determined using a colorimetric assay based on the method of Zhishen et al. (1999). The extract (50 μ l) was mixed in a microplate with equal amounts of NaNO_2 , AlCl_3 and NaOH (final concentrations 0.4%, 0.8%, and 2%, respectively). Absorbance was measured at 510 nm, and the results were expressed in mg of catechin equivalents (CE) per 100 g of FW. Anthocyanin content was determined by the pH-differential method (Giusti and Wrolstad, 2001). The extract (50 μ l) was diluted with potassium chloride buffer at pH 1.0 and with sodium acetate buffer at pH 4.5, to reach final concentrations of 0.02% and 0.32%, respectively. The diluted solutions were then kept at room temperature for 15 min, and the absorbance was read

at 520 and 700 nm. The results were expressed as mg of cyanidin-3-glucoside (C3GE) per 100 g FW by using a molar absorptivity coefficient (ϵ) of 26900. The antioxidant capacity was measured using the 1,1-diphenyl-2-picrylhydrazyl (DPPH) method adapted from Brand-Williams et al. (1995). The method consisted of mixing 30 μ l of diluted extract with DPPH to a final concentration of 0.005%. The reaction was allowed to stand for 60 min in darkness at room temperature. Absorbance was measured at 535 nm, and the results were expressed in mg of Trolox equivalents (TE) per 100 g of FW.

2.4. Polyphenols analysis

One hundred micrograms of internal standard (methyl 4-hydroxybenzoate) was added to an aliquot of 4 ml of the polyphenol extract, which was concentrated to dryness by speed vac at 45°C. After the addition of 1 ml of the mixture of MeOH/formic acid (95:5 v/v), the solubilized polyphenolic extract was filtered (RC 0.2 μ m Phenomenex, Le Pecq, France), and 1 μ L was directly injected into a Waters Acquity UPLC equipped with a photodiode array detector (280, 330, and 520 nm) and a Waters Acquity HSS T3 column (100 mm $\times$ 2.1 mm i.d., 1.8 μ m) protected by a precolumn filter (Waters), which was housed in a 45°C heated oven. The identification of the phenolic compounds was also achieved through the coupling of a Waters Acquity UPLC with an ion trap mass spectrometer Bruker Daltonics HCT ultra equipped with an electrospray ionization source. Details about the separation, characterization and quantification of phenolic compounds were previously described by Aubert et al. (Aubert et al., 2014).

2.5. Sugar and acid determinations

Sugar and acid extracts were filtered (RC 0.2 μ m Phenomenex) and directly injected into the UPLC with a photodiode array detector (210 nm) and a refractive index (RI) detector connected in series, and an ion exclusion Rezex ROA-Organic H⁺ column (300

mm × 7.8 mm) protected by a Carbo-H guard column (Phenomenex), which was housed in a 27°C heated oven. The separation, characterization and quantification of sugars and organic acids were carried out as previously described by Aubert et al. (2014).

2.6. Mineral analysis

Fresh pulp tissue (5 g) and peel tissue (3 g) for each cultivar were lyophilized (Cryodos-50, Telstar, Terrassa, Spain) for approximately 3 days to constant dried weight. Then, the fresh/dry weight ratio was calculated, and the samples were ground to a fine powder. The mineral composition was determined using the methods of C.I.I. (1969). Total nitrogen was determined by Dumas method AOAC 990.03 (FP528, Leco Corporation, MI, USA). Briefly, three hundred milligrams of dried tissue were digested with nitric acid-hydrogen peroxide (67%-30%) using a high performance microwave digestion unit (ETHOS One, Milestone Srl, Sorisole, Italy). From the extract, phosphorus was determined spectrophotometrically (UNICAM Helios, Thermo Spectronic, Cambridge, UK) by the phospho-vanadate colorimetric method at 430 nm. Potassium, sodium, calcium, magnesium, iron, copper, manganese and zinc were analyzed from the same convenient diluted extract by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Activa-M, Horiba Jobin Yvon SAS, Longjumeau, France). Contents for all elements were expressed as mg per 100 g dry weight (DW).

2.7. Statistical analyses

The statistical analysis was performed using SPSS 23.0 (SPSS, Inc.; Chicago, IL). For each genotype, three biological replicates were considered to calculate the mean and standard error (SE) for each parameter. Data were evaluated by analysis of variance (two-way and one-way ANOVA) to determine the significance of tissue, cultivar and, interaction (tissue × cultivar) for the linear model. When analysis of variance showed

significant differences ($P \leq 0.05$), means were separated by Duncan's multiple range tests. A Student t test ($P \leq 0.05$) was run to compare mineral composition on both pulp and peel tissues. Pearson correlation coefficients were calculated to compare analytical determinations and techniques to reveal significant association between traits at $P \leq 0.05$. Principal component analysis (PCA) was performed using Statbox 7.2.2 (FBC Software).

3. Results and discussion

3.1. *Antioxidant compound contents determined by spectrophotometry*

Contents of ascorbic acid, total phenolic, flavonoid and anthocyanin, and relative antioxidant capacity, in peel and pulp of the nine peach cultivars harvested in 2015 are reported in Table 2. Two-way ANOVA revealed significant variations ($P \leq 0.05$) depending on the fruit tissue (peel and pulp) and cultivar studied. For all antioxidant compounds, peel tissue showed significantly higher contents than those determined in pulp. Significant cultivar $\times$ fruit tissue interactions were found for all antioxidant contents.

In peel, the ascorbic acid content varied from 10.43 mg /100 g FW in Crown Princess to 33.26 mg /100 g FW in Calanda Tardio. Total phenolic content (TPC) ranged from 88.89 to 277.29 mg GAE/100 g FW, flavonoids varied from 39.32 to 245.37 mg CE/100 g FW and RAC ranged from 133.05 to 401.31 mg TE/100 g FW. Among cultivars, the Calanda Tardio showed the highest contents for all antioxidants except anthocyanins. The ascorbic acid and total phenolic contents as investigated in the present study were found to be in the same range reported by Gil et al. (2002) in the peels of yellow-flesh peaches and nectarines. Finally, the total anthocyanin values varied from 0.55 mg

C3GE/100 g FW in Calanda Tardio to 17.63 mg C3GE/100 g FW in Big Top. Only Big
 Top, Venus, and Baby Gold 9 cultivars contain anthocyanins in both peel and pulp
 tissues. Depending on the peach cultivar, the peel tissue had 2-3 times higher contents
 of antioxidant compounds compared to the pulp. These results agree with previous
 studies reporting phytochemical contents in peel and pulp tissues of peach fruit (Gil et
 al., 2002; Liu et al., 2015; Manzoor et al., 2012b; Vizzotto et al., 2007). However, this
 is the first report achieved evaluating antioxidant contents in peel tissue in these nine
 cultivars. For the pulp, the ascorbic acid contents ranged from 4.15 to 14.16 mg /100 g
 FW, with the highest contents in Venus and the lowest in Big Top and Crown Princess.
 Contents for ascorbic acid were in the same range as those previously reported for peach
 (Abidi et al., 2015; Abidi et al., 2011; Font i Forcada et al., 2013; Gil et al., 2002;
 Tavarini et al., 2008). The limit ranges of total phenolic content (25.13 to 139.07 mg
 GAE/100 g), flavonoids (8.18 to 111.95 mg CE/100 g FW) and RAC (22.7 to 194.1 mg
 TE/100 g FW) were found to be maximum in the Spanish cultivar Calanda Tardio and
 minimum for nectarines (Big Top and Venus), and for the Tebana cultivar. Furthermore,
 the values of TPC and flavonoids of the Spanish peach Calanda Tardio and Miraflores
 were found to be higher than those reported by Font i Forcada et al. (2014), probably
 due to the optimization of the methodology minimizing interfering compounds in this
 food matrix. The Spanish cultivar, Calanda Tardio had the highest contents of TPC,
 flavonoids and RAC, in peel and pulp tissues, which has never been reported in the
 literature.
 Furthermore, in both peel and pulp tissues, high and significant correlations ($P \leq 0.01$)
 were found between RAC and TPC ($r=0.995$ in peel and $r=0.950$ in pulp) , and between
 RAC and flavonoid content ($r=0.980$ in peel and 0.981 in pulp) (Table S2); these

findings were in part consistent with previous studies in pulp (Abidi et al., 2011; Gil et al., 2002; Liu et al., 2015). In addition, TPC was highly correlated ($P \leq 0.01$) with flavonoids ($r=0.989$ in peel and $r=0.986$ in pulp), which indicates that flavonoids are an important group of phenolic compounds in peach fruit (Abidi et al., 2011; Cantín et al., 2009; Font i Forcada et al., 2013). On the contrary, we did not find correlation between anthocyanins and RAC (Table S2) as other authors have found in red-fleshed peach and plum (Vizzotto et al., 2007). We may probably conclude that this may be due to the low content of anthocyanins found in the studied yellow-fleshed peach cultivars.

3.2. Polyphenol contents determined by UPLC-MS

In the present study, 12 phenolic compounds, including 5 hydroxycinnamic acids, 3 flavan-3-ols, 3 flavonols, and 1 anthocyanin (cyanidin-3-O-glucoside) were identified by UPLC-MS and quantified by UPLC-DAD in the peel and pulp of nine peach cultivars (see chromatogram in Fig. S2). These results are consistent with previous studies reporting the concentration of polyphenol compounds in peach fruit (Aubert et al., 2014; Tomás-Barberán et al., 2001; Zhao, et al., 2015). The composition and content of phenolic compounds detected in both peel and pulp of peaches are shown in Table 3 and Figure S3. In general, peel contained significantly higher concentrations of phenolic compounds than those quantified in pulp tissue. The flavonols were exclusively located in the peel of peach fruit, as reported by other studies (Scordino et al., 2012; Zhao, et al., 2015). The individual flavonols, quercetin-3-galactoside (FO1), quercetin-3-O-glucoside plus quercetin-3-O-rutinoside (FO2) and kaempferol-3-O-glucoside (FO3), represent 7.8% of the total polyphenols content in peel tissue (Fig. S4). Chlorogenic acid (HA3) was the major hydroxycinnamic acid in the studied cultivars, followed by neochlorogenic acid (HA1), and it was detected in significantly higher amounts in peel

than that in pulp. The hydroxycinnamic acids, which are the major compounds of polyphenols, were significantly correlated ($P \leq 0.01$) with total polyphenols in peel ($r=0.976$) and in pulp ($r=0.999$) (Table S2). The major flavanols detected in peel and pulp were catechin (FA2) and procyanidin dimer B1 (FA1), as reported by Chang et al. (2000).

In peel tissue, total polyphenols contents ranged from 10.50 to 45.06 mg/100 g FW within the studied peach cultivars. Total flavonols ranged from 0.71 to 2.76 mg/100 g FW, with higher contents in Venus, Baby Gold 9 and Calanda Tardio than in the other cultivars. The Spanish cultivar Calanda Tardio showed the highest amount of total polyphenolic and hydroxycinnamic acids, while Tebana exhibited the lowest content. Values of total hydroxycinnamic acid content were within the range reported by other authors (Tomás-Barberán et al., 2001). The level of cyanidin-3-glucoside (ANT1), responsible for the red color detected in peel was high as reported previously (Aubert et al., 2014; Tomás-Barberán et al., 2001; Zhao, et al., 2015), being higher in Big Top with 4.89 mg/100 g FW than in the rest of cultivars. The total flavanols ranged from a low 0.26 mg/100 g FW in Big Top to a high 1.58 mg/100 g FW in Calanda Tardio. Our results showed a clear distinction among cultivars for phenolic contents in peel, which indicated a potential application of phenolic profile to select cultivars rich in polyphenols.

For the pulp, total polyphenol content ranged from 3.62 in Tebana to 19.37 mg/100 g FW in the Spanish cultivars Calanda Tardio. The total hydroxycinnamic acid concentrations, varied from 3.45 mg/100 g FW in Tebana to 18.09 mg/100 g FW in Calanda Tardio. The chlorogenic acid (HA3) content in pulp was noticeably higher than neochlorogenic acid (HA1) for all cultivars except for Calante and Calanda Tardio,

which contain 1.2- and 1.6-fold more HA1 than HA3, respectively. Less than 0.13 mg/100 g FW of cyanidin-3-glucoside (ANT1) content was also detected in pulp of four cultivars (Table 3).

3.3. *Comparison of analytical techniques*

As expected, the content of total polyphenols quantified by UPLC-DAD mirrored those detected by spectrophotometry. These findings were confirmed with the significant correlation between flavanols *versus* flavonoids ($r=0.923$; $P\leq 0.01$) and total polyphenols *versus* TPC in both peel ($r=0.918$; $P\leq 0.01$) and pulp ($r=0.942$; $P\leq 0.01$) tissues (Fig. S5, Table S2). The highly significant correlation ($r=0.997$; $P\leq 0.01$) between cyanidin-3-glucoside and total anthocyanins, which were quantified by UPLC-DAD and spectrophotometry, respectively, supports the same indication. In general, the spectrophotometric method overestimates the phenolic content due to interferences with the non-phenolic constituents, but in our experiment, we cannot compare values because units are based on Equivalents of a specific standard (Escarpa and González, 2001; Tabart et al., 2010).

The high correlations found between contents of phenolic compounds quantified by spectrophotometry and UPLC-DAD attest that both analytical methods provide comparable results. The spectrophotometry method is fast, simple and cheaper, and it allows the analysis of a larger number of samples at the same time. However, to identify individual polyphenols or perform authenticity profiles in peach fruits, the UPLC-MS method is required.

3.4. *Sugar and acid content determined by UPLC-DAD*

Sugar and organic acid contents in pulp and peel tissues of the nine peach cultivars are shown in Table 4. For sugar content, two-way ANOVA revealed a significant

interaction (fruit tissue $\times$ cultivar) only for sucrose and sorbitol contents. As a consequence, one-way ANOVA was performed individually for the fructose, glucose and total sugar contents of each tissue. The analysis showed significant differences among cultivars in pulp, but no difference was detected in peel. Sugar contents were higher in pulp than in peel, and sucrose was the main sugar found in both tissues. In pulp, sucrose was followed by fructose, glucose and sorbitol as the main sugars, as reported by other authors previously (Abidi et al., 2015; Aubert et al., 2014).

In pulp, total sugar contents varied from 10.75 to 15.70 g/100 g FW, where the Spanish cultivar Calanda Tardio and the nectarine Big Top showed the highest levels. Sucrose contents in pulp ranged from 8.64 to 11.5 g/100 g FW, being highest in Big Top, followed by Baby Gold 9, Calanda Tardio, Miraflores and Venus, which had quite similar values. The mean contents of fructose and glucose were higher in Calanda Tardio and Venus than those found in the rest of the cultivars. Cirilli et al. (2016), reported that in commercial cultivars the concentration of fructose and glucose tended to be stable across ripening, with a ratio from 0.8 to 1; however, we have found that this ratio ranged from 1.1 to 1.2. For peel, the sucrose content was also higher in the nectarine Big Top (7.71 g/100 g FW) and in the Tebana peach (7.35 g/100 g FW). Concerning sorbitol content, Calanda Tardio showed the highest value in pulp and peel with 2.98 g/100 g FW and 1.97 g/100 g FW, respectively. Remarkably, Big Top was the only cultivar that contains more sorbitol in peel than in pulp. Sorbitol is the sugar alcohol that is mainly related to peach aroma and taste, along with other carbohydrates and organic acids (Colaric et al., 2005).

The individual sugars (sucrose, glucose, fructose and sorbitol) were analyzed separately, as they affect mouth-feel attributes and aroma perception; in particular, the sweetness

intensity depends on the specific sugar profile (Cirilli et al., 2016; Colaric et al., 2005; Robertson et al., 1988). In this work, contents for all individual sugars in Calanda Tardio contributed to give this cultivar the highest content for total sugar, while, in Big Top, only sucrose was the main contributor to sweetness.

Three organic acids were quantified in both pulp and peel tissues. Malic acid was found as the major acid followed by quinic and citric acids in both tissues; the contents of these acids were significantly higher in pulp than in peel, except for quinic acid, which was found predominantly in peel. In immature fruits, malic and quinic acid concentrations are high, but they decrease during fruit maturation; however, citric acid reaches maximum contents at intermediate maturities (Wu et al., 2005). Two-way ANOVA showed significant fruit tissue $\times$ cultivar interaction for all organic acid contents.

In the pulp, total organic acid contents varied from 0.59 to 1.42 g/100 g FW, the values were in the same range reported by Bassi and Selli (1990). The cultivars, Venus, Calanda Tardio, Crown Princess and Calante had the highest amounts of total organic acids. Malic acid ranged from 0.40 to 1.03 g/100 g FW and was significantly higher in Calanda Tardio. In contrast, the content of quinic acid was quite similar among cultivars, ranging from 0.11 to 0.27 g/100 g FW. The cultivar Venus contained the highest amount of citric acid (0.41 g/100 g FW), which represents the second most abundant acid (28.7% of the total organic acid) in this cultivar. The values of the individual organic acids in pulp seem to be within the range reported by Reig et al., (2013). In peel, total organic acids varied from 0.34 g/100 g FW in Baby Gold 9 to 0.92 g/100 g FW in Venus. In general, peach cultivars had relatively the same malic acid content, ranging from 0.15 to 0.46 g/100 g FW. Quinic acid content varied from 0.11 in

Calante to 0.45 g/100 g FW in Crown Princess. Finally, citric acid content was found rather similar among cultivars, varying from 0.03 to 0.13 g/100 g FW. These findings are of relevance because no data on sugar and acid concentrations in peach peel has been reported so far. Additionally, as it was mentioned above, depending on the cultivar, the peel is an excellent source of nutritional metabolites and a good source of energy.

3.5. *Principal component analysis (PCA)*

A principal component analysis (PCA) was performed to graphically summarize the distribution of the 24 variables (ascorbic acid, total phenolic, flavonoid and anthocyanin contents, relative antioxidant capacity, and contents of sugar, organic acid, and polyphenol) within the peel and pulp tissues of the nine commercial peach cultivars. As shown in Fig. 1A, 71% of the total variance was explained by the first two axes. The first axis (PC1), 47% of the variance explained, mainly discriminates the peel from the pulp samples, whereas the second axis (PC2), 24% of the variance explained, mainly discriminates samples of Calanda Tardio cultivar (CT) from the others. The distribution of the variables is shown in Fig. 1B. Except for sorbitol (SOR), procyanidin dimer B2 (FA3), citric (CIT) and quinic acid (QUI), most of variables are well represented on the first two axes. As shown, peel samples positively correlated on PC1 are particularly characterized by high levels of caffeoylquinic acid derivative (HA5), chlorogenic acid (HA3), glycosides of quercetin (FO1, FO2) and kaempferol (FO3), (+)-catechin (FA2), ascorbic acid (AA), relative antioxidant capacity (RAC), total phenolic (TPC), flavonoid (FLA) and anthocyanin contents (ANT). Regarding pulp samples, negatively correlated on the first axis, they are rather defined by high levels of sucrose (SUC), glucose (GLU), fructose (FRU) and malic acid (MAL). Calanda Tardio samples,

positively correlated on PC2, are mainly characterized by high levels of sorbitol (SOR), p-coumaroylquinic acid (HA2), chlorogenic acid derivatives (HA1, HA4) and lower levels of anthocyanin content (ANT), cyanidine-3-glucoside (ANT1) and quinic acid (QUI).

3.6. Mineral contents

To complete the study about the nutritional value of peach fruits and to compare tissue compartmentation, separate mineral analyses were carried out in peel and pulp tissues from the nine cultivars. The mineral compositions of the pulp and peel of peach fruit from the cultivars studied are presented in Figure 2. The analyses revealed that potassium was the predominant element in both peach tissues. As shown in Figure 2, peel tissue had significantly higher contents of nitrogen, calcium, magnesium, iron and manganese than pulp; these results are similar to those reported by Manzoor et al. (2012a). These elements are known for their food value in human nutrition; potassium contributes to the maintenance of cell organization and permeability, calcium plays an important role in the growth of skeletal tissue as well as in the metabolic regulations of biomolecules as coenzymes, and magnesium is involved in nervous system stability and muscle contraction. Regarding micronutrients, elements required in small amounts in the human diet, iron is present as the predominant micronutrient in peel. Iron is the most important element in the prevention of anemia, and it is a core element of red blood cells (Ismail et al., 2011).

4. Conclusion

The present work appeared to be the first comparative and detailed study reported on the antioxidant compounds, profiles of sugars, organic acids and polyphenols in peel and

pulp in peach cultivars, including foreign and Spanish non-melting peaches as well as nectarines. This study clearly established that the peach peel is an excellent source of nutritional metabolites and mineral elements (K, Ca, Mg, Fe, etc.), and can be also a good source of energy. The peel, which is generally regarded as wastes with little value in the peach fruit industry may be valorized for canning uses or processed products as a source of antioxidant compounds for nutraceutical applications. Taking into account that peaches have approximately 7-9% of peel tissue and that exocarp is a concentrated source of nutrients, we can assume that over 20% of the total phytochemical concentration of a peach is lost if the peel is discarded and not consumed. Furthermore, these results show that the traditional Spanish non-melting peach cultivars, in particular Calanda Tardio (late-maturing), are rich in antioxidant compounds and have a great potential for human health and nutrition. The differences found among the studied cultivars revealed singular properties for each cultivar to be considered in future breeding programs to enhance a particular bioactive compound related to human health.

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Supplementary material

There are 2 Supplementary Tables and 5 Supplementary Figures.

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Table 1. Characteristics of the nine peach cultivars: Cultivar name, origin, fruit characteristics and harvest day for 2015.

Cultivars	Origin	Fruit type	Flesh type	Stone type	Harvest day
Crown Princess	USA	Peach	Non-melting	Cling	19-june
Big Top	USA	Nectarine	Melting	Cling	01-july
Tebana	Italy	Peach	Non-melting	Cling	01-july
Venus	Italy	Nectarine	Melting	Free	05-aug
Andross	USA	Peach	Non-melting	Cling	07-aug
Baby Gold 9	USA	Peach	Non-melting	Cling	26-aug
Miraflores	Spain	Peach	Non-melting	Cling	14-sept
Calanda Tardio	Spain	Peach	Non-melting	Cling	07-oct
Calante	Spain	Peach	Non-melting	Cling	07-oct

Table 2. Ascorbic acid, TPC, flavonoid and anthocyanin contents and RAC in peel and pulp of nine peach cultivars harvested in 2015.

Cultivars	Fruit tissue	Ascorbic acid	TPC	Flavonoids	Anthocyanins	RAC
	Peel	17.95 b	142.68 b	111.38 b	5.53 b	201.95 b
	Pulp	9.63 a	59.47 a	40.47 a	0.37 a	78.11 b
	Signification	***	***	***	***	***
Crown Princess	Peel	10.43 cd	137.00 ef	107.05 h	9.01 c	186.91 ef
	Pulp	5.27 a	44.44 b	30.04 bc	nd	56.2 ab
Big Top	Peel	23.18 j	88.89 d	39.32 b-d	17.63 d	133.05 cd
	Pulp	4.15 a	25.13 a	8.18 a	0.28 a	23.25 a
Tebana	Peel	13.30 fg	102.15 d	69.63 ef	2.50 b	155.96 c-e
	Pulp	9.12 bc	28.02 a	9.59 a	nd	22.7 a
Venus	Peel	10.78 c-e	122.81 e	87.25 fg	9.07 c	170.84 de
	Pulp	14.16 gh	37.63 ab	21.31 ab	0.24 a	45.04 ab
Andross	Peel	25.5 k	140.37 f	116.79 hi	1.09 ab	195.02 ef
	Pulp	12.48 ef	71.26 c	41.11 cd	nd	80.93 b
Baby Gold 9	Peel	18.88 i	162.48 g	129.23 i	7.84 c	218.83 f
	Pulp	7.62 b	64.38 c	43.79 cd	0.65 ab	76.82 b
Miraflores	Peel	11.02 de	131.55 ef	107.36 h	1.03 ab	183.37 ef
	Pulp	11.44 de	63.5 c	45.67 cd	nd	78.98 b
Calanda Tardio	Peel	33.26 l	277.29 h	245.37 j	0.55 ab	401.31 g
	Pulp	10.40 cd	139.07 f	111.95 hi	nd	194.1 ef
Calante	Peel	15.2 h	121.61 e	100.45 gh	1.09 ab	172.26 de
	Pulp	12.04 d-f	61.84 c	52.61 de	nd	125 c
Interaction	Signification	***	***	***	***	***

Two-way ANOVA was performed for lineal model on raw data followed by Duncan's test. Significance: at *** $P \leq 0.001$. Values in the same column followed by different letters were significantly different at $P \leq 0.05$, ascorbic acid (AsA) = mg AsA/100 g FW, total phenolic content (TPC) = mg GAE/100 g FW, gallic acid equivalents (GAE), flavonoids = mg CE/100 g FW, catechin equivalents (CE), anthocyanins = mg C3GE /100 g FW, cyanidin-3-glucoside relative (C3GE), antioxidant capacity (RAC) = mg TE/100 g FW, Trolox equivalents (TE), non-detected (nd).

Table 3. Polyphenolic compounds content (mg/100 g FW) in the peel and pulp of nine peach cultivars harvested in 2015.

Cultivars	Fruit tissue	Flavonols				Hydroxycinnamic acids					
		FO1	FO2	FO3	FO	HA1	HA2	HA3	HA4	HA5	HA
	Peel	0.49	0.93	0.23	1.65	2.82 a	0.07	13.23 b	0.24 b	0.46 b	16.81 b
	Pulp	nd	nd	nd	nd	3.45 b	0.07	4.17 a	0.17 a	0.04 a	7.90 a
	Signification					***	NS	***	***	***	***
Crown Princess	Peel	0.54 c	0.89 b	0.08 a	1.51 b	2.03 a-c	0.07 d-g	11.84 ef	0.20	0.30 bc	14.43 fg
	Pulp	nd	nd	nd	nd	2.14 a-c	0.04 a-d	5.43 cd	0.17	0.05 a	7.82 b-d
Big Top	Peel	0.75 d	1.12 c	0.08 a	1.96 c	1.02 a	0.03 ab	10.47 ef	0.08	0.39 de	11.98 ef
	Pulp	nd	nd	nd	nd	1.21 ab	0.02 a	3.38 a-c	0.03	0.05 a	4.68 ab
Tebana	Peel	0.25 ab	0.37 a	0.22 ab	0.84 a	1.14 a	0.04 a-e	6.74 d	0.09	0.25 b	8.27 cd
	Pulp	nd	nd	nd	nd	1.02 a	0.02 a	2.35 a	0.03	0.04 a	3.45 a
Venus	Peel	0.53 c	1.84 e	0.40 e	2.76 d	3.04 c	0.11 hi	11.60 ef	0.18	0.45ef	15.38 g-k
	Pulp	nd	nd	nd	nd	2.11 a-c	0.09 gh	2.58 ab	0.09	0.03 a	4.90 a-c
Andross	Peel	0.33 b	0.49 a	0.25 c	1.08 a	2.29 a-c	0.07 d-g	9.97 e	0.20	0.33 cd	12.86 e-g
	Pulp	nd	nd	nd	nd	2.63 c	0.03 a-c	5.09 cd	0.12	0.04 a	7.91 b-d
Baby Gold 9	Peel	0.73 d	1.65 e	0.33 d	2.71 d	2.11 a-c	0.05 b-f	14.37 g	0.20	0.57 g	17.31 jk
	Pulp	nd	nd	nd	nd	2.27 a-c	0.07 e-g	4.02 a-c	0.11	0.04 a	6.52 a-c
Miraflores	Peel	0.36 b	0.30 a	0.16 b	0.82 a	2.53 bc	0.06 c-f	10.59 ef	0.25	0.41 ef	13.83 e-h
	Pulp	nd	nd	nd	nd	3.37 c	0.07 fg	3.36 a-c	0.18	0.03 a	7.02 bc
Calanda Tardio	Peel	0.78 d	1.38 d	0.28 cd	2.44 d	7.98 e	0.12 i	31.19 h	0.70	0.98 h	40.98 l
	Pulp	nd	nd	nd	nd	10.73 f	0.13 i	6.61 d	0.56	0.05 a	18.09 k
Calante	Peel	0.16 a	0.31 a	0.24 ab	0.71 a	3.19 c	0.07 d-g	12.28 f	0.26	0.48 f	16.28 g-k
	Pulp	nd	nd	nd	nd	5.54 d	0.14 i	4.71 b-d	0.28	0.05 a	10.71 de
Interaction	Signification	***	***	***	***	***	***	***	NS	***	***

Table 3. (continued)

Cultivars	Fruit tissue	Flavanols				ANT1	TPP
		FA1	FA2	FA3	FA		
	Peel	0.52 b	0.57 b	0.04 b	1.13 b	1.54 b	21.13 b
	Pulp	0.32 a	0.31 a	0.02 a	0.65 a	0.03 a	8.59 a
	Signification	***	***	***	***	***	***
Crown Princess	Peel	0.59 c-f	0.74 f	0.04 d	1.37 fg	2.85 c	20.15 f-h
	Pulp	0.09 a	0.38 b-d	0.04 d	0.51 bc	0.02 a	8.35 b-d
Big Top	Peel	0.04 a	0.12 a	0.10 e	0.26 ab	4.89 d	19.09 e-g
	Pulp	0.03 a	0.10 a	0.02 ab	0.15 a	0.09 a	4.92 ab
Tebana	Peel	0.37 bc	0.45 b-d	0.03 cd	0.86 c-e	0.53 a	10.50 cd
	Pulp	0.04 a	0.11 a	0.01 ab	0.17 ab	nd	3.62 a
Venus	Peel	0.51 a-c	0.80 f	0.03 c-e	1.34 fg	2.65 bc	22.13 gh
	Pulp	0.33 b	0.31 b	0.02 a-c	0.66 cd	0.13 a	5.69 ab
Andross	Peel	0.77 f	0.68 ef	0.04 cd	1.48 fg	0.23 a	15.65 e
	Pulp	0.33 b	0.31 b	0.02 ab	0.66 cd	nd	8.57 b-d
Baby Gold 9	Peel	0.58 c-f	0.54 de	0.04 d	1.17 ef	2.28 b	23.47 h
	Pulp	0.38 bc	0.38 b-d	0.02 ab	0.78 cd	0.05 a	7.34 a-c
Miraflores	Peel	0.65 d-f	0.66 ef	0.02 a-c	1.33 fg	0.12 a	16.11 e
	Pulp	0.43 bc	0.33 bc	0.01 a	0.77 cd	nd	7.79b-d
Calanda Tardio	Peel	0.77 f	0.76 f	0.04 d	1.58 g	0.07 a	45.06 i
	Pulp	0.73 cf	0.50 cd	0.04 d	1.27 fg	nd	19.37 e-g
Calante	Peel	0.38 bc	0.38 b-d	0.02 a-c	0.78 cd	0.24 a	18.01 ef
	Pulp	0.55 c-e	0.36 bc	0.02 ab	0.92 de	nd	11.63 d
Interaction	Signification	***	**	***	**	***	***

Two-way ANOVA was performed for lineal model on raw data followed by Duncan test. ** $P \leq 0.01$, *** $P \leq 0.001$ and NS indicates not significant. Values in the same column followed by different letters were significantly different at $P \leq 0.05$. Abbreviations: neochlorogenic acid (HA1), p-coumaroylquinic acid (HA2), chlorogenic acid (HA3), 4-caffeoylquinic acid (HA4), caffeoylquinic acid derivative (HA5), Total hydroxycinnamic acids (HA), procyanidin dimer B1 (FA1), (+)-catechin (FA2), procyanidin dimer B2 (FA3), Total flavanols (FA), cyanidin-3-glucoside (ANT1), quercetin-3-O-galactoside (FO1), quercetin-3-O-galactoside + quercetin-3-O-rutinoside (FO2), kaempferol-3-glucoside (FO3), Total flavonols (FO), Total polyphenols (TPP), non-detected (nd).

Table 4. Sugar and organic acid contents in pulp and peel of nine peach cultivars harvested in 2015.

Cultivars	Fruit tissue	Sugars (g/100 g FW)				Total Sugars	Organic acids (g/100 g FW)			Total Acids
		Sucrose	Fructose	Glucose	Sorbitol		Malic	Quinic	Citric	
	Pulp	9.84 b	1.17 b	1.02 b	0.91	12.94 b	0.66 b	0.16 a	0.12 b	0.94 b
	Peel	5.21 a	0.78 a	0.60 a	0.80	7.39 a	0.35 a	0.25 b	0.06 a	0.66 a
	Signification	***	***	***	NS	***	***	***	***	***
Crown Princess	Pulp	8.64 b-d	1.06 a	0.90 ab	0.15 a	10.75 a	0.73 d	0.27 bc	0.11 bc	1.10 ef
	Peel	4.87 a	0.71	0.54	0.15 a	6.26	0.37 bc	0.45 d	0.04 ab	0.86 c-e
Big Top	Pulp	11.5 e	1.05 a	0.95 ab	0.91 bc	14.45 d	0.43 bc	0.17 ab	0.10 a-c	0.71 b-d
	Peel	7.71 bc	0.59	0.44	1.46 d	10.19	0.40 bc	0.37 cd	0.06 ab	0.82 cd
Tebana	Pulp	9.43 cd	1.03 a	0.87 a	0.17 a	11.50 ab	0.51 c	0.11 a	0.08 a-c	0.70 b-d
	Peel	7.35 b	0.98	0.70	0.24 a	9.27	0.42 bc	0.35 c	0.06 ab	0.83 cd
Venus	Pulp	9.71 de	1.38 c	1.25 d	1.03 cd	13.37 c	0.86 d	0.15 a	0.41 d	1.42 g
	Peel	5.33 a	0.94	0.72	1.08 cd	8.06	0.46 c	0.33 c	0.13 c	0.92 de
Andross	Pulp	9.65 c-e	1.20 b	1.02 bc	0.68 a-c	12.54 bc	0.40 bc	0.14 a	0.06 ab	0.59 a-c
	Peel	5.25 a	0.82	0.60	0.43 ab	7.10	0.26 ab	0.21 ab	0.03 a	0.51 ab
Baby Gold 9	Pulp	10.24 de	1.23 b	1.06 c	0.41ab	12.94 c	0.43 bc	0.16 a	0.08 a-c	0.66 b-d
	Peel	4.20 a	0.75	0.53	0.30a	5.77	0.15 a	0.15 a	0.04 ab	0.34 a
Miraflores	Pulp	9.81de	1.12 ab	0.98 ab	0.98 b-d	12.88 c	0.74 d	0.13 a	0.09 a-c	0.96 de
	Peel	4.5a	1.38	0.54	0.88 bc	6.62	0.38 bc	0.14 a	0.08 a-c	0.60 a-c
Calanda Tardio	Pulp	10.06 de	1.38 c	1.29 d	2.98 f	15.70 e	1.03 e	0.17 ab	0.09 a-c	1.29 fg
	Peel	4.16 a	0.86	0.79	1.97 e	7.79	0.40 bc	0.14 a	0.05 ab	0.59 a-c
Calante	Pulp	9.48 cd	1.07 a	0.91 ab	0.87 bc	12.32 bc	0.81 d	0.14 a	0.08 a-c	1.02ef
	Peel	3.56 a	0.67	0.54	0.65 a-c	5.42	0.27 ab	0.11 a	0.05 ab	0.43ab
Interaction	Signification	*	NS	NS	*	NS	***	***	***	***

Two-way ANOVA was performed for lineal model on raw data followed by Duncan's test. Significance $*P \leq 0.05$, $***P \leq 0.001$ and NS indicates not significant. Values in the same column followed by different letters were significantly different at $P \leq 0.05$. FW: fresh weight.

Table S1. Physico-chemical traits evaluated in the nine peach cultivars harvested in 2015.

Cultivars	Harvest date	Fruit weight	Firmness	SSC	TA	pH	SSC/TA
Crown Princess	170	182.51	28.67 b	10.7	0.71	3.75	15.05
Big Top	182	196.85	41.26 d	18.3	0.44	4.42	41.78
Tebana	182	127.59	32.56 bc	12.5	0.42	4.29	29.90
Venus	217	267.60	17.64 a	15.7	1.09	3.62	14.39
Andross	219	170.10	35.23 c	14.9	0.35	4.30	41.16
Baby Gold 9	238	201.58	35.72 c	14.0	0.44	4.10	31.75
Miraflores	257	183.00	32.93 bc	14.2	0.68	3.79	21.01
Calanda Tardio	280	162.52	64.44 f	17.7	0.92	3.59	19.26
Calante	280	285.65	46.94 e	13.8	0.76	3.67	18.18

Units and abbreviations: Harvest date =Julian days; Fruit weight (g); Firmness (N); N=Newton; SSC=Soluble solids content (°Brix); FW= Fresh weight; TA=Titrateable acidity (g malic acid/100 g FW). For firmness different letters are significant different at $P<0.05$.

Table S2. Pearson's correlation coefficients between pairs of antioxidant compounds in peel and pulp of fruits harvested in 2015 (N=9).

	Tissue	Flav	RAC	HA	FA	C3GE	TPP
TPC	Peel	0.989**	0.995**	0.957**	ns	ns	0.918**
	Pulp	0.986**	0.950**	0.937**	0.886**	ns	0.942**
Flav	Peel	-	0.980**	0.928**	0.694*	ns	0.864**
	Pulp	-	0.981**	0.972**	0.923**	ns	0.971**
ANT	Peel		ns	ns	ns	0.997**	ns
	Pulp		ns	ns	ns	ns	ns
RAC	Peel		-	0.966**	ns	ns	0.921**
	Pulp		-	0.972**	0.931**	ns	0.978**
HA	Peel			-	ns	ns	0.976**
	Pulp			-	0.855**	ns	0.999**
FA	Peel				-	ns	ns
	Pulp				-	ns	0.875**

Total Phenolic Content (TPC) = mg GAE/100 g FW, flavonoids (Flav) = mg CE/100 g FW, anthocynins (ANT) = mg C3GE/100 g FW, cyanidin-3-glucoside equivalent (C3GE) = mg/100 g FW, relative antioxidant capacity (RAC) = mg TE/100 g FW, Trolox equivalents (TE), total polyphenols (TPP) = mg/100 g FW, total hydroxycinnamic acids (HA) = mg/100 g FW, Total flavanols (FA) = mg/100 g FW. Significance: ** $P \leq 0.01$, ns not significant.

Fig. 1. Results from PCA analysis: (A) projection of the samples (○, pulp; ●, peel; CP, Crown Princess; BT, Big Top; TE, Tebana; VE, Venus; AN, Andross; BG, Baby Gold 9; MI, Miraflores; CT, Calanda Tardio; CA, Calante); (B) factor loadings of variables (contents of AA, ascorbic acid; TPC, total phenolic content; FLA, flavonoid; ANT, anthocyanin; RAC, relative antioxidant capacity; HA1, neochlorogenic acid; HA2, p-coumaroylquinic acid; HA3, chlorogenic acid; HA4, 4-caffeoylquinic acid; HA5, caffeoylquinic acid derivative; FA1, procyanidin dimer B1; FA2, (+)-catechin; FA3, procyanidin dimer B2; ANT1, cyanidin-3-glucoside; FO1, quercetin-3-O-galactoside; FO2, quercetin-3-O-galactoside + quercetin-3-O-rutinoside; FO3, kaempferol-3-glucoside; SUC, sucrose; GLU, glucose; FRU, fructose; SOR, sorbitol; MAL, malic acid; CIT, citric acid; QUI, quinic acid).

Fig. 2. Mineral concentrations (mg/100 g DW) for major nutrients, secondary nutrients and micronutrients in peel and pulp tissues of peach fruits harvested in 2015. Significant differences between pulp and peel at *** $P \leq 0.001$; ** $P \leq 0.01$ and * $P \leq 0.05$; ns: not significant (Student's t test).

Fig. S1. Calibration curves with their corresponding standard for ascorbic acid, total phenolic compounds, flavonoids and relative antioxidant capacity. Data are mean $\pm$ SD of 3 replicates.

Fig. S2. UPLC chromatograms of polyphenol compounds found in pulp (A), and peel (B) of Calanda Tardio peaches detected at 280 nm. Peaks: 1. neochlorogenic acid (HA1); 2. procyanidin dimer B1 (FA1); 3. (+)-catechin (FA2); 4. p-coumaroylquinic acid (HA2); 5. chlorogenic acid (HA3); 6. 4-Caffeoylquinic acid (HA4); 7. procyanidin dimer B2 (FA3); 8. caffeoylquinic acid derivative (HA5); IS. methyl 4-hydroxybenzoate (internal standard); 9. quercetin-3-O-galactoside (FO1); 10. quercetin-3-O-galactoside + quercetin-3-O-rutinoside (FO2); 11. kaempferol-3-glucoside(FO3).

Fig. S3. Polyphenolic composition in peel and pulp of nine peach cultivars harvested during 2015 (FO: flavonols; ANT1: cyanidin-3-glucoside; FA: flavan-3-ol; HA: hydroxycinnamic acids).

Fig. S4. Percentage of the main polyphenols in peel of nine peach cultivars harvested during 2015.

Fig. S5. Linear regression between analytical techniques (HPLC and spectrophotometry) for polyphenolic determinations.

Significance: $^{**}P \leq 0.01$ and $^{*}P \leq 0.05$.