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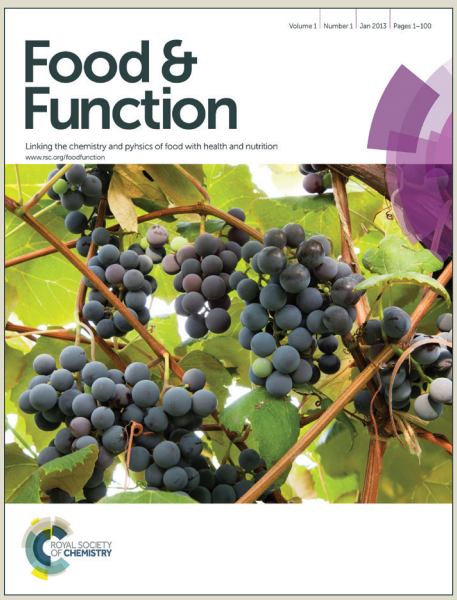

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Assessment of the distribution of phenolic compounds and contribution to the antioxidant activity in Tunisian figs leaves, fruits, skins and pulps using mass spectrometry-based analysis.

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Abstract

The phenolic composition of leaves, fruits, skins and pulps from two *F. carica* cultivars, 'Temri' and 'Soltani', was studied in order to understand its contribution to the antioxidant activity. A total of 116 compounds were characterized based on the results obtained by reversed-phase ultra-high performance liquid chromatography coupled to diode array and mass spectrometry detection. In general, the leaves of both cultivars and the skin of 'Soltani' presented richer qualitative profiles compared to the other plant parts. Using the negative ionization mode, qualitative profiles of the same part of the studied figs were similar. In this regard, rutin was the main compound in fruits, skins and leaves, but with different relative amounts. Alternatively, an isomer of prenylhydroxygenistein was the major compound in the pulps. In the positive ionization mode, 9 anthocyanins were characterized in 'Soltani' skin, only two of them being also present in the green cultivar 'Temri'. The main anthocyanins were cyanidin 3-rutinoside and cyanidin 3,5-diglucoside, depending on the cultivar and fruit part. In this ionization mode, 14 furanocoumarins were also detected in the leaves of both studied cultivars with methoxypsoralen and psoralen being the most relatively abundant. In addition, our findings showed a good correlation between the antioxidant activity, total phenol content, and abundance of some phenolic subfamilies such as hydroxybenzoic acids, flavonols, flavones, hydroxycoumarins and furanocoumarins with $r > 0.97$.

Keywords:

Anthocyanins; antioxidant activity; *Ficus carica*; furanocoumarins; Moraceae; RP-UHPLC-DAD-QTOF-MS; phenolic compounds.

Introduction

Moraceae is a family with widespread distribution in the tropics and subtropics, but it also occurs in temperate regions.[1] This family includes well-known plants such as figs, banyans, breadfruits, mulberries, and osage-oranges.[2] *Ficus* constitutes one of the thirty-seven geniuses of this family, with about 800 species.[3] Among them, *F. carica* (fig tree or common fig) is one of the oldest known fruits crop, which is used for fruit production.[4] Alongside the olive trees, *F. carica* is considered a biomarker of the Mediterranean ecosystem, its fig fruits are also consumed fresh, dried, preserved, canned, and candied.[5]

Phenolic compounds are secondary metabolites biosynthesized by plants both during normal development and in response to stress conditions.[6] Polyphenols significantly contribute to the organoleptic properties of fruits: colour, bitterness and astringency.[7] Furthermore, these minor compounds could be beneficial for human health.[8] Several researches on *F. carica* have shown changes in the figs phenolic composition as a consequence of the cultivar,[8,9] drying or extraction method,[5,10,11] pollinization,[4] sampling date and maturation.[5,12] Other studies have focused on particular phenolic classes, such as anthocyanins in fig fruits[9,13] and furanocoumarins in leaves.[10] Interestingly, *F. carica* exhibits antiplatelet, antispasmodic and anti-inflamatory activity,[14] but little is known about their active compounds and qualitative and quantitative differences in *F. carica* plant parts. In this regard, some authors have attributed these beneficial properties to the presence of phenolic compounds, although it has not been demonstrated in depth.[9,13]

Conventionally, the phenolic content is evaluated through colorimetric methods. However, these studies should be complemented with more specific and selective analytical methodologies in order to fully understand the relationship between the phenolic composition and health.[15] In addition, these novel analytical techniques may be useful in order to identify new sources of phenolic compounds that are underused or usually disposed of as waste

material in many food processing industries, such as leaves or fruit peels.[16] The analytical techniques used to study *F. carica* includes gas chromatography coupled to mass spectrometry (MS) and a flame ionization detector (FID),[12] as well as liquid chromatography (LC) coupled to UV/Vis or diode array detection (DAD) and mass spectrometry (MS) in a negative or positive ionization mode depending on the target phenolic class.[10,11,13,17–19] As commented above, the composition of phenolic compounds is not only influenced by the cultivar, but also varies depending on the part studied.[18] In this context, Solomon *et al.*[9] described differences in total anthocyanins and total phenol content between whole fresh fruits, pulps and skins of commercial fig cultivars using mainly spectrophotometric methods. Dueñas *et al.*[13] showed qualitative and quantitative differences of anthocyanins in pulps and skins from Spanish fig cultivars. Oliveira *et al.*[20] found quantitative differences between pulps, skins and leaves of Portuguese fig cultivars, but their study only focused on seven target compounds.

Therefore, the objective of this study was to evaluate the phenolic distribution in different parts of two Tunisian fig cultivars 'Temri' and 'Soltani' and give new insights into its contribution to the antioxidant activity using MS-based analysis. To achieve this, dried leaves, whole fruits, skins and pulps were extracted using solid-liquid extraction and analyzed concisely by reversed phase (RP)-ultra-high-performance liquid chromatography (UHPLC) coupled to DAD and MS, using a quadrupole-time-of-flight (QTOF) mass analyzer. Moreover, the total phenol content and the antioxidant activity by means of three *in vitro* assays were assessed.

Results and discussion

Selection of the extraction procedure

The first step of the study was to choose an extraction procedure that enabled to recover the maximum amounts of phenolic compounds, but by using the minimum volume of organic solvent and extraction time. In this way, two solid-liquid extraction procedures were tested: a conventional maceration with an ethanolic-aqueous solution (extraction method 1) and an extraction with a methanolic-aqueous solution assisted by an extensive grounding with an Ultraturrax blender and ultrasounds (extraction method 2). In general, our findings showed that the total phenol content (TPC) and antioxidant activity were slightly higher using the extraction method 2, whereas the yield was lower in comparison with method 1 (Fig. 1). Furthermore, the qualitative phenolic profiles using both methods were similar. As an example, Fig. S1 (supplementary information) show the base peak chromatogram (BPC) in the negative ionization mode of leaves extracted using the previous methods. These results could be explained by the fact that the solubility of phenolic compounds is quite comparable in both solvents that present similar polarity.[21] Moreover, an exhaustive grounding and a sonication step favored the extraction of phenolic compounds like in previous studies on different vegetal parts, such as chickpea seeds, lettuce leaves and eggplant fruits, that enable shorting the extraction time.[22–24] Interestingly, since ethanol is not as toxic as methanol, the conventional extraction method could be used to prepare bioactive extracts for further *in vivo* studies, but requiring a higher dosage considering the yield, and the second one is interesting for finding key active compounds in a faster and cheaper way.

Phenolic profiling *via* UV-Vis and accurate MS and MS/MS data

The metabolic profiling of the aqueous-methanolic extracts of leaves, fruits, skins and pulps of both Tunisian figs cultivars was performed by using RP-UHPLC-DAD-QTOF-MS and -MS/MS, and electrospray ionization. The UV/Vis was a valuable tool for a preliminarily classification phenolic compounds, whereas MS and MS/MS allowed their molecular formula and fragmentation patterns to be obtained. When possible, the proposed compounds were

confirmed with standards, by comparing the RT, UV/Vis data and MS/MS fragmentation pattern. Table 1 shows the general results for 91 phenolic compounds detected using the negative ionization mode (analytical method 1), for the following: retention time (RT), experimental *m/z* (monoisotopic ion), molecular formula, main MS/MS fragments, the ionization mode and the proposed assignment. That includes hydroxybenzoic acids, hydroxycinnamic acids, flavonoids (flavonols, flavones, flavanones, flavanonols, flavanols and isoflavones), and hydroxycoumarins. In general, the UV absorption maximums (Table S1) in these families agree with previous studies.[25–27] In the same way, Table 2 shows the results about anthocyanins (9), furanocoumarins (15) and a isoflavone, since most of them could be only detected by using the positive (analytical method 2) under our analytical conditions. In this case, the Vis and UV data (Table S2) of anthocyanins and furanocoumarins were also in agreement with the literature.[10,13,28,29] In addition to UV data, Tables S1 and S2 provide additional details for the characterization studies in the negative and positive ionization modes, respectively, such as species, plant family, and also in previous studies which identified these compounds. Furthermore, Fig. S2 depicts representative chromatograms of the studied parts of the cultivar 'Soltani': the base peak chromatogram in the negative ionization mode (A-D) and the UV chromatograms at 520 (E-H) and 254 nm (I-L), representing selected absorption wavelengths of anthocyanins and furanocoumarins, respectively.

Our characterization steps could be basically summarized by a targeted searching of previously known fig phenolic compounds, an untargeted analysis and a predictive study of unreported phenolic structures based on all the spectroscopic data obtained by the detection techniques applied. In this way, 33 phenolic compounds characterized in the negative and positive ionization modes were previously cited in the literature of *F. carica* (Tables S1 and S2). However, by using our methodology, a major number of isomers were found, for

example, isomers of caffeoyl quinic acid, ferulic acid, luteolin *C*-hexoside *C*-pentoside, apigenin *C*-hexoside *C*-pentoside, cyanidin rutinoside and marmesin.[8,11,13,20,30] The stereochemical differentiation between these isomers was not possible with our methodology.

In order to continue the characterization of the rest of unidentified peaks, all data provided by RP-UHPLC-DAD-QTOF-MS and -MS/MS were investigated in depth, as well as the literature concerning Moraceae and other plant families. As an example, Fig. S3 shows the comparison of apigenin and vanillic acid standards and those found in the analysis of *F. carica*. As depicted, the standards and these compounds presented the same RT, molecular formula, UV maximums, as well as fragmentation pattern, and thus enabling their unequivocally identification. The flavonoid apigenin was found in other *Ficus* species such as *F. formosana* and *F. hirta.*[31] The UV absorption spectra showed a main absorption band close to 336 nm (Fig. S3A), which is in accordance with the findings of Lin *et al*.[25] The MS/MS ions' product at *m/z* 241.0492, 227.0351 and 225.0539 may be attributed to the loss of CO, CO-CH_2 and CO_2, respectively, from the C ring of the precursor ion. Several retro Diels-Alder (RDA) fragments such as the product ions' at *m/z* 151.0035 ($^{1,3}A^-$) and 149.0245 ($^{0,2}A^-$) were also observed. Additionally, we noted that $^{1,3}A^-$ ions systematically underwent further CO_2 loss leading to an ions' fragment at *m/z* 107.0139 (Fig. S3B and C). This fragmentation pattern was in accordance with previous studies.[27,32,33] Another example is shown in Fig. S3D-F, i.e. vanillic acid. This hydroxybenzoic acid showed UV maximums at 261 and 292 nm (Fig. S3D).[34,35] As a characteristic, the main ions' product were at *m/z* 152.0121, due to the loss of CH_3 from the methoxy group of the aglycone, and at *m/z* 123.0431 that represents the typical decarboxylation of phenolic acids (Fig. S3E and F).[23] This compound was previously described in Moraceae family.[31] Therefore, since the method proved enough reliability for the characterization, the rest of the compounds were either

matched in depth with standards when possible or alternatively characterized by matching our data with previous studies.

Finally, some unreported structures of phenolic compounds (see Table S1 and S2) could be predicted according to their spectroscopy data and compared to well-characterized ones in our samples. This enabled us to predict modifications such as the conjugation with malic acid or sugars (hexose deoxyhexose and pentose) as well as the dimerization. As an example, Fig. 2 depicts a general procedure for the characterization of a new dimer of cyanidin rutinoside and petunidin in the skin of 'Soltani', which has not been previously reported. In this manner, Fig. 2A shows the chromatographic peaks detected above 520 nm, which is a characteristic of anthocyanins, and highlights that one corresponding to the novel dimer. The mass spectrum at the elution time of that peak is showed in Fig. 2B, where different ions were observed. Among them, the ion with a *m/z* value of 911.2244 ($[M]^+$) presented a molecular formula of $C_{43}H_{43}O_{22}^+$ and a putative structure containing cyanidin based on its MS/MS spectrum (Fig. 2C). According to previous studies, this ion is caused by a neutral quinoidal base and a flavylium cation in the dimeric anthocyanin.[36] Whereas other authors suggest other possibilities including an A-type flavanflavylium and a B-type flavene-flavylium.[13] In agreement with these studies, the MS/MS spectrum (Fig. 2C) showed the neutral loss of rutinose (308.1117 u) as well as petunidin to release the cyanidin aglycone at *m/z* 287.0542. Other fragments ions related to petunidin fragmentation were also found, *m/z* 571.0881 and *m/z* 477.0804, which corresponded to the loss of CH_4O from the methoxy group and phloroglucinol from the A ring, respectively, and *m/z* 435.0710 after the RDA cleavage of the C ring. The production of ions from the fragmentation of cyanidin aglycone ion were similar to those found in the rest of cyanidin derivatives (Table 2 and S2) as in to a previous study.[37] Further spectroscopic studies are thus required to confirm this preliminary predicted structure.

These characterization results remark the interest of using a RP-UHPLC coupled to DAD and a high resolution QTOF mass analyzer to characterize phenolic compounds and predict structures before to the application of other spectroscopic tools, in accordance with our previous study.[33] In this sense, most studies on the distribution of these phytochemicals in *F. carica* determined up to eight phenolic compounds belonging to phenolic acids, flavonols, flavanols or furanocoumarins using RP-HPLC coupled to UV-Vis detection.[16,20] Alternatively, Dueñas *et al.*[13] determined 15 anthocyanins in skins and pulps of several figs cultivars by using RP-HPLC coupled to DAD and an ion trap mass analyzer *via* electrospray ionization in the positive mode.

Total phenolic content

In general, leaves were significantly richer ($p < 0.05$) in the TPC than whole fruits, the TPC value being the highest in the cultivar 'Soltani' (1.05 g of gallic acid/100 g of sample; Fig. 3A). Among the fruit parts, a clear and statistically significant difference ($p < 0.05$) was found for the skin of 'Soltani' (0.32 g of gallic acid/100 g of sample; Fig. 3B). In agreement with Solomon *et al.,*[9] this fact could be explained since the mature skins from the 'Soltani' fruits have purple colour externally, whereas 'Temri' skins fruits are yellowish green. In contrast, the TPC value in 'Temri' pulps (0.26 g of gallic acid/100 g of sample; Fig. 3B) was slightly higher compared with the fruits of the same cultivar and the pulps of cultivar 'Soltani'. The TPC of the whole fruit was lower than the dark-coloured cultivar 'Mission', in fresh[9] or dry basis[38], but higher than fresh fruits of other fig cultivars.[9,39]

***In vitro* antioxidant activity**

A complete set of antioxidant assays was performed in order to fully estimate the antioxidant potential of the studied *F. carica* parts and cultivars: trolox equivalent antioxidant capacity (TEAC) or ABTS method, ferric ion reducing antioxidant power (FRAP), and oxygen radical absorbance capacity (ORAC). The results are described in Fig. 3A, to compare

222 between leaves and the whole fruit, while in Fig. 3B presents a comparison between the
223 different fruit parts. According to our TPC data, leaves of the two studied cultivars showed
224 high antioxidant activity values. In the same manner, the highest TEAC, FRAP as well as
225 ORAC values were measured in 'Soltani' leaves, being 4.03 mmol of Trolox equivalents/100
226 g of sample, 4.06 mmol of Fe^{2+} equivalents/100 g of sample and 2.16 mmol of Trolox
227 equivalents/100 g of sample, respectively. Furthermore, 'Soltani' skins were the major
228 contributing tissues to the total of the antioxidant activity in comparison with the other fruit
229 parts, with values of TEAC, FRAP and ORAC equal to 1.04 mmol of Trolox
230 equivalents/100g of sample, 1.43 mmol of Fe^{2+} equivalents/100 g of sample and 0.46 mmol of
231 Trolox equivalents/100g of sample, respectively. The differences between fruit parts from the
232 green cultivar 'Temri' were not as clear as in the cultivar 'Soltani'. In this regard, previous
233 studies have also stated that skins were the main contributors to fruits in terms of phenolic
234 compounds[9,11] or antioxidant activity,[9,39] especially in cultivars such as 'Negra de Mesegar' or
235 'Mission' that are also characterized by darker external colours.

236 **Relationship between the phenolic composition of *F. carica* plant parts and the**
237 **antioxidant activity**

238 Overall, our results indicated a significant correlation between the TPC of *F. carica*
239 plant parts and the antioxidant activity by either electron or hydrogen transfer mechanism:
240 TEAC ($r = 0.973$), FRAP ($r = 0.985$) and ORAC ($r = 0.974$) (Table 3). There is also a
241 significant correlation in the antioxidant activity determined by these three methods ($r > 0.97$;
242 Table 3).

243 This linear regression analysis was also carried out to compare the correlation between
244 the abundance of the phenolic subfamilies determined by MS and the antioxidant activity. In
245 this way, positive correlations ($r > 0.90$) (Table 3) were noticed for hydroxybenzoic and
246 hydroxycinnamic acids, flavonols, flavones, isoflavones, hydroxycoumarins, and

247 furanocoumarins. Therefore, leaves of both cultivars, especially those from 'Soltani',
248 possessed the strongest antioxidant activity that is explained by the occurrence of high
249 amounts of phenolic compounds and, in particular, a high abundance of these phenolic
250 families or subfamilies. In contrast, there was a poor correlation between the antioxidant
251 activity and the abundance of flavanones, flavanols and flavanonols.

252 In addition, Tables 1 and 2 show the relative amounts of the phenolic compounds
253 determined by MS, as a preliminary way to understand their individual contribution. To our
254 knowledge, there are not enough studies that compare the antioxidant properties and phenolic
255 content in plant parts by using such a concise characterization study. Interestingly, a common
256 feature was observed: the flavonol quercetin-3-*O*-rutinoside (rutin) was the main individual
257 representative in all *F. carica* parts using the negative ionization mode (Table 1). This finding
258 was in agreement with a study by Vallejo *et al.*,[11] except for pulps. This compound is widely
259 spread in plants and, as our results showed, an important contributor to the antioxidant
260 activity ($r > 0.96$, Table 3). In contrast, pulps from both cultivars presented higher relative
261 amounts of prenylhydroxygenistein with quite similar relative areas (Table 1). As far as we
262 know, there are no previous studies reporting the presence of this compound in fig pulps.
263 Since pulps represent the most consumed fig parts, these compounds are expected to be key
264 markers of their consumption.

265 Other interesting phenolic family was linear furanocoumarins, which were mostly
266 constituted by leaves. Among them, psoralen and methoxypsoralen presented the main
267 relative areas (Table 2), followed by oxypeucedanin hydrate in 'Temri' and prenyl
268 methoxypsoralen in 'Soltani' (Table 2). In this regard, furanocoumarins were one of the main
269 active antioxidants of plant materials from *Ruta graveolens* (fam. Rutaceae)[40] and *Angelica*
270 *dahuricae* (fam. Umbelliferae) roots.[41] The abundance of the main furanocoumarins, psoralen

and methoxypsoralen, also correlated significantly with the antioxidant activity values ($r > 0.97$, Table 3), especially with ORAC.

A general rule is that *O*-glycosylation seems decreasing the antioxidant capacity of flavonoids by reducing free hydroxyls and metal chelation sites,[42,43] whereas *C*-glycosylation may improve the antioxidant capacity of flavones.[44] In this respect, *C*-glycoside flavones were the main representative of this phenolic subclass in all fig parts. As an example, the abundance of apigenin *C*-hexoside *C*-pentoside (isomer II) was highly correlated with the antioxidant activity ($r > 0.96$, Table 3), leaves being the richest part. Other interesting substitution is the prenylation that may increases the bioactivity of flavonoids.[45] We found some prenylated phenolic compounds in all fig parts, including prenylated isoflavones. However, in the case of the major one, prenylhydroxygenistein (isomer III), the correlation between its abundance and the antioxidant activity was significant, but weaker than the above mentioned compounds ($0.889 < r < 0.919$, Table 3).

Regarding fruit parts, the skins of 'Soltani' were qualitatively and quantitatively richer in anthocyanins (Table 2). A slight positive correlation was found between their abundance and the antioxidant activity, especially higher for TEAC ($r > 0.83$) (Table 3). Among this flavonoid subclass, the main anthocyanin was an isomer of cyanidin rutinoside as described in other fig cultivars.[13] The abundance of the latter also showed a moderate correlation with the antioxidant activity of fruit parts (Table 3). Previous studies have shown that cyanidin aglycone is a powerful antioxidant, which is comparable to quercetin aglycone, and at the same time higher than other flavonoid aglycones and phenolic acids.[43,46] Other interesting phenolic modification was found in this flavonoids subfamily: a putative anthocyanin dimer in 'Soltani' that was present in the whole fruits and skins but with very little amounts. The occurrence of this type of biflavonoid as well as other anthocyanins dimer products was firstly

295 reported in red wines and then in plant tissues.[13] However little is known about the impact on
296 the antioxidant activity.

297 Overall, leaves and skins of *F. carica* are quite interesting phenolic sources not only
298 for their antioxidant activity compared to the other plant parts, but also for their complex
299 qualitative composition. In particular, leaves were characterized by the presence of
300 furanocoumarins and other phenolic compounds such as *C*-glycosides flavones and
301 isoflavones that were not reported in leaves of other plant families. Further studies are thus
302 demanded to understand the antioxidant potential of each individual phenolic compound as
303 well as their synergism or antagonism effects.

304

305 ## Conclusions

306 Overall, a total of 116 phenolic compounds were characterized, being differently
307 distributed among the studied parts. Among them, a new dimer of cyanidin rutinoside and
308 petunidin was found in 'Soltani' skins, being reported for the first time in our study. In
309 comparison with fruits or their parts, leaves of both cultivars, followed by 'Soltani' skins,
310 presented richer phenolic qualitative profiles with also higher total phenol content and
311 antioxidant activity. These observations were not only in accordance with the presence of
312 furanocoumarins in leaves and anthocyanins in skins but also with the abundance of certain
313 phenolic types, such as hydroxybenzoic and hydroxycinnamic acids, flavonols, flavones,
314 isoflavones and hydroxycoumarins. The latter showed a clear positive correlation with the
315 antioxidant activity. In addition, the cultivar 'Soltani' was of special interest since its phenolic
316 composition and antioxidant activity have not been reported until the present study. In this
317 sense, dried leaves of both cultivars and skins of 'Soltani' fruit, when discarded, may present
318 a high potential for further valorization in pharmacology and cosmetology.

319 ## Experimental

Chemical and reagents

Methanol, acetonitrile, formic acid and glacial acetic acid were purchased from Fisher Chemicals (ThermoFisher, Waltham, MA, USA). Solvents used for extraction and analysis were of analytical and HPLC-MS grades, respectively. Ultrapure water was obtained by a Milli-Q system (Millipore, Bedford, MA, USA). The reagents used to measure the TPC and the antioxidant capacity were Folin & Ciocalteu's, sodium carbonate (Na_2CO_3), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AAPH), 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) diammonium salt, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (trolox), fluorescein, potassium persulphate ($K_2S_2O_8$) and ferric sulphate ($FeSO_4$). They were purchased from Sigma–Aldrich (St. Louis, MO, USA). Dehydrated sodium phosphate, trihydrated sodium acetate, sodium acetate, ferric chloride ($FeCl_3 \cdot 6H_2O$) and hydrochloric acid were obtained from Panreac (Barcelona, Spain). Phenolic standards available in our laboratory were bought from Sigma-Aldrich. Degree of purity of standards was around 95% (w/w).

Fig samples

Leaves and fruits from the *F. carica* cultivars 'Temri' and 'Soltani' were collected in the region Sfax region (southeast Tunisia) in August 2013. The sample (about 0.5 kg) was randomly harvested and immediately transferred to the laboratory where the skins were peeled manually with a knife, without including the fruit pulp. Leaves, whole fruit, skin and pulp (including seeds) were dried in the shade at room temperature at 30°C for 10 days, and then were finely ground prior to extraction.

Preparation of the extracts

The extraction of phenolic compounds from the fig parts was based on two different procedures. In the extraction method 1 each fig part (3 g) was put in amber glass bottles, homogenized in 100 mL of 70:30 (v/v) ethanol/water solution by using a stirring hot plate for

345 24 hours at 37 °C and 150 rpm. Each mixture was centrifuged at 8000 rpm for 15 min and the
346 supernatant collected. Afterwards, the solvent was put in a rotary evaporator under vacuum at
347 40 °C, until dryness and the residue was redissolved in ethanol/water, 70:30 (v/v).[33] In the
348 extraction method 2 each fig part was treated with methanol/water solution 80:20 (v/v)
349 according to the extraction procedure described elsewhere[47] with some modifications. In brief,
350 each fig part (0.5 g) was placed in a test tube and 20 mL of methanol/water (80:20, v/v) was
351 added, sonicated for 30 min and then centrifuged at 8000 rpm for 15 min. After
352 centrifugation, the supernatant was collected and the precipitate was re-extracted following
353 the same previous steps. The two supernatants were then combined, the solvent was put in a
354 rotary evaporator under vacuum at 40 °C until dryness and the residue redissolved in
355 methanol/water solution 80:20 (v/v).

356 Finally, the supernatants were filtered with a syringe filter (regenerated cellulose, 0.2
357 μm pore size) and stored at −20 °C until analysis. The extraction was repeated twice for each
358 fig part and cultivar.

359 **Total phenol content and antioxidant capacity assays**

360 The TPC of the extracts was determined in triplicate by the colorimetric assay using
361 the Folin–Ciocalteu reagent,[48] modified according to Romero-de Soto *et al.*[49] The TEAC
362 assay was based on Miller *et al.*'s approach,[50] but following the modification described by
363 Laporta *et al.*[51] The FRAP assay was conducted following the method described by Benzie
364 and Strain[52], whereas the ORAC assay was based on Ou *et al.*[53] and modified by Laporta *et*
365 *al.*[51] Blanks and trolox or ferric sulphate curves were conducted using the same solvents as
366 those used for the extracts. All the procedures are detailed in the supplementary information.
367 Caffeic acid was used as control with the following values per mmol: TEAC value, 1.04 ±
368 0.08 mmol equivalents of Trolox[46]; FRAP value, 2.19 ± 0.07 mmol equivalents of Fe^{2+}[54], and
369 ORAC value, 4.22 ± 0.24 mmol equivalents of Trolox[53].

Analyses by RP-UHPLC−DAD-QTOF-MS and –MS/MS

Analyses were made with an Agilent 1200 series rapid resolution (Palo Alto, CA, USA) equipped with a binary pump, an autosampler and a DAD. The system was coupled to a 6540 Agilent Ultra-High-Definition (UHD) Accurate-Mass Q-TOF LC/MS, which was equipped with an Agilent Dual Jet Stream electrospray ionization (Dual AJS ESI) interface. Two analytical methods were used to perform the characterization work according to our previous study.[33] In the analytical method 1 the mobile phases consisted of a water-0.5% acetic acid solution (mobile phase A) and acetonitrile (mobile phase B). Moreover, to improve the analysis of anthocyanins and furanocoumarins, the mobile phases consisted of a water-0.5% formic acid solution (phase A) and acetonitrile (phase B) (analytical method 2). A multistep linear gradient was then applied in both cases: 0 min, 0% B; 10 min, 20% B; 15 min, 30% B; 20 min, 50% B; 25 min, 75% B; 30 min, 100% B; 31 min, 100% B; 34 min, 0% B; 40 min, 0% B. The flow rate was set at 0.50 mL/min throughout the gradient. Separation was carried out with a Zorbax Eclipse Plus C18 column (150 × 4.6 mm, 1.8 μm of particle size) at room temperature. The UV spectra were recorded from 190 to 600 nm. The injection volume was 5 of μL, all samples being injected at the same initial weight/volume ratio.

The operating conditions in negative ionization mode were as follows: gas temperature, 325 °C; drying gas, nitrogen at 10 L/min; nebulizer pressure, 20 psig; sheath gas temperature, 400 °C; sheath gas flow, nitrogen at 12 L/min; capillary voltage, 4000 V; skimmer, 45 V; octapole radiofrequency voltage, 750 V; focusing voltage, 500 V, with an automatically set the corresponding polarity. In the case of the analytical method 2, MS analyses were performed in positive ionization mode, with the parameters set as previously mentioned, but with the corresponding polarity. Spectra were acquired over a mass range from *m/z* 100 to 1700 except for MS^2 experiments which was performed from *m/z* 70 to 1700. Reference mass correction of each sample was performed with a continuous infusion of

Agilent TOF mixture containing two mass references for each ionization mode. The detection window was set to 100 ppm. Data acquisition (2.5 Hz) in the profile mode was governed *via* the Agilent MassHunter Workstation B.05.01.

Data analysis was performed on a Mass Hunter Qualitative Analysis B.06.00 (Agilent technologies). For characterization, the isotope model selected was common organic molecules with a peak spacing tolerance of m/z 0.0025 and 7 ppm. Then, the compounds' characterization was done by taking into account the generation of molecular formula candidate with a mass error limit of 5 ppm. It was also performed by taking into consideration and also considering RT, experimental and theoretical masses, and MS/MS spectra. The MS score related to the mass error, isotope abundance and isotope spacing for the generated molecular formula, was set at ≥80. Confirmation was made through standards' comparison with samples, whenever they were available. Consequently, Moraceae literatures as well as several chemical structure databases were consulted: PubChem, ChemSpider, SciFinder Scholar, Reaxys, Phenol-Explorer, KNApSAcK Core System, and Metlin.

Statistical analysis

Pearson's linear correlations and the one-way analysis of variance (ANOVA) test followed by the Student-Newman-Keuls post-hoc test were performed using IBM SPSS Statistics 22 (Armonk, NY, USA). Microsoft Excel 2007 (Redmond, WA, USA) was also employed for statistical analysis.

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Conflicts of interest

The authors declare no competing financial interest.

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Figure captions

Figure 1. Comparison of the yield (g/g), total phenol content (TPC) (g of gallic acid/100 g of sample) and antioxidant activity of leaves and fruits from *F. carica* cultivar 'Temri' extracted with two different protocols (see the experimental section). The antioxidant activity was evaluated by: trolox equivalent antioxidant capacity (TEAC) (mmol equivalents of Trolox/100 g of sample), ferric ion reducing antioxidant power (FRAP) (mmol equivalents of Fe^{2+}/100 g of sample) and oxygen radical absorbance capacity (ORAC) (mmol equivalents of Trolox/100 g of sample). Data are given as mean ± standard deviation. For each of the studied parameters, values with different letters are significantly different at $p < 0.05$.

Figure 2. (A) UV chromatograms at 520 nm of 'Soltani' skins, (B) MS spectra for this region highlighting the *m/z* value of the dimer of petunidin-cyanidin rutinoside and (C) its main MS/MS fragments.

Figure 3. Bar graph representing the total phenol content (TPC) (mg of gallic acid/100 g of sample) and antioxidant activity of (A) leaves and whole fruits, and (B) whole fruits, skins and pulps from *F. carica* cultivars 'Temri' and 'Soltani'. The antioxidant activity was evaluated by: trolox equivalent antioxidant capacity (TEAC) (mmol equivalents of Trolox/100 g of sample), ferric ion reducing antioxidant power (FRAP) (mmol equivalents of Fe^{2+}/100 g of sample) and oxygen radical absorbance capacity (ORAC) (mmol equivalents of Trolox/100 g of sample) assays. Data are given as mean ± standard deviation. For each of the studied parameters, values with different letters are significantly different at $p < 0.05$.

Figure captions (supplementary information)

Figure S1. Example of the qualitative comparison of 'Temri' leaves extracted by two different protocols (see the experimental section) and analyzed by RP-UHPLC-DAD-QTOF-MS in the negative ionization mode. The intensity of the base peak chromatograms (BPC) was normalized to the largest area of both chromatograms.

Figure S2. Chromatographic profiles of the leaves, fruits, skins and pulps from *F. carica* cultivar 'Soltani' obtained by RP-UHPLC-DAD-QTOF-MS: base peak chromatogram (BPC) in negative ionization mode using analytical method 1 (A-D) and UV chromatograms at 254 (E-H) and 520 nm (I-L) using the analytical method 2.

Figure S3. Examples of the UV (A and D) and MS/MS spectra highlighting the main fragments of commercial standards of (B) apigenin and (E) vanillic acid compared with those found in *F. carica*, (C) apigenin and (F) vanillic acid.

Table 1. Phenolic compounds characterized using the negative ionization mode in the studied parts from *F. carica*.

RT[a] (min)	[M-H]$^-$	Formula	Score	Error (ppm)	I[a]	Main fragments *via* MS/MS	Phenolic compound	Relative abundance (%)							
								TL[a]	TF[a]	TS[a]	TP[a]	SL[a]	SF[a]	SS[a]	SP[a]
Hydroxybenzoic acids and derivatives								**12.30**	**29.60**	**15.77**	**27.14**	**13.32**	**24.76**	**15.29**	**18.25**
10.71	359.0997	$C_{15}H_{20}O_{10}$	96.5	-3.8	N	197.0455; 179.0346; 153.0549; 135.0452; 85.0292	Syringic acid hexoside I	0.06	-	-	-	0.03	-	-	-
10.76	315.0726	$C_{13}H_{16}O_9$	97.6	-5.1	N	153.0194; 152.0114; 109.0293; 108.0293	Dihydroxybenzoic acid hexoside I	0.15	2.13	2.00	1.47	0.16	2.49	1.36	1.27
10.76	313.0571	$C_{13}H_{14}O_9$	84.1	-1.7	N	197.0348; 167.0351; 153.0560; 135.0454; 133.0141; 123.0454; 115.0038	Syringic acid malate I	0.15	-	-	-	0.24	-	-	-
10.86	359.0988	$C_{15}H_{20}O_{10}$	95.1	-2.1	N	197.0455; 179.0344; 153.0557; 135.0452; 123.0450; 85.0290	Syringic acid hexoside II	0.05	-	-	-	0.04	-	-	-
11.07	329.0882	$C_{14}H_{18}O_9$	95.3	-2.7	N	167.0348; 152.0115; 123.0447; 108.0215	Vanillic acid glucoside	0.06	8.00	0.72	11.39	0.05	6.23	0.50	6.51
11.08	475.1456	$C_{20}H_{28}O_{13}$	84.5	-0.1	N	329.0879; 167.0356; 109.0294	Vanillic acid hexoside deoxyhexoside	0.05	-	0.10	-	0.04	-	0.10	-
11.13	313.0570	$C_{13}H_{14}O_9$	84.2	-1.7	N	179.0327; 135.0451; 133.0141; 115.0031	Syringic acid malate II	0.03	-	-	-	0.04	-	-	-
11.20	433.0986	$C_{17}H_{22}O_{13}$	96.7	-0.2	N	301.0521; 169.0139; 168.0069; 151.0036; 125.0241	Gallic acid di-pentoside I	0.04	-	-	-	0.03	-	-	-
11.23	315.0720	$C_{13}H_{16}O_9$	99.6	0.7	N	153.0188; 109.0293	Dihydroxybenzoic acid hexoside II	0.04	0.72	0.30	0.98	0.03	0.64	0.31	0.44
11.51	433.0990	$C_{17}H_{22}O_{13}$	96.4	-1.0	N	301.0564; 169.0137; 168.0062; 151.0035; 125.0243	Gallic acid di-pentoside II	0.61	0.22	0.21	0.37	0.46	0.37	0.24	0.20
11.59	447.1152	$C_{18}H_{24}O_{13}$	92.0	-2.1	N	315.0719; 271.0816; 152.0113; 109.0293; 108.0216	Dihydroxybenzoic acid hexoside pentoside I	0.16	0.32	0.27	0.17	0.42	0.28	0.12	0.08
12.32	447.1143	$C_{18}H_{24}O_{13}$	97.4	0.2	N	152.0114; 109.0291	Dihydroxybenzoic acid hexoside pentoside II	0.03	0.65	0.20	0.39	0.06	0.39	0.18	0.15
12.50	153.0197	$C_7H_6O_4$	85.6	-2.2	N	109.0293; 108.0217	Dihydroxybenzoic acid	0.03	5.32	3.40	3.88	0.14	3.26	1.91	2.97
12.52	315.0721	$C_{13}H_{16}O_9$	97.3	0.0	N	153.0194; 152.0194; 109.0291; 108.0219	Dihydroxybenzoic acid hexoside III	0.05	-	-	-	0.11	-	-	-
12.62	285.0620	$C_{12}H_{14}O_8$	93.8	-2.0	N	153.0196; 152.0117; 109.0297; 108.0218	Dihydroxybenzoic acid pentoside I	1.27	3.57	4.18	4.06	1.68	4.19	6.14	1.94
12.74	447.1142	$C_{18}H_{24}O_{13}$	96.3	0.5	N	153.0181; 152.0114; 109.0291; 108.0216	Dihydroxybenzoic acid hexoside pentoside III	0.18	-	0.32	-	0.42	0.34	0.16	0.17

13.09	417.1053	$C_{17}H_{22}O_{12}$	95.1	-3.2	N	285.0613; 241.0715; 153.0165; 152.0115; 108.0218; 109.0294	Dihydroxybenzoic acid di-pentoside	8.98	4.51	2.76	1.85	8.96	4.21	3.61	1.53
13.10	285.0620	$C_{12}H_{14}O_8$	97.4	-1.9	N	153.0193; 152.0108; 109.0293; 108.0218	Dihydroxybenzoic acid pentoside II	0.06	0.08	0.05	0.10	0.05	0.11	0.09	0.10
14.67	137.0240	$C_7H_6O_3$	96.5	2.6	N	109.0294; 108.0216; 93.0336; 92.0268	Hydroxybenzoic acid I	0.25	-	0.32	-	0.27	-	0.18	-
15.10	137.0240	$C_7H_6O_3$	86.0	2.7	N	93.0343	Hydroxybenzoic acid II	0.03	1.29	0.26	0.45	0.04	0.55	0.11	0.78
15.91	167.0349	$C_8H_8O_4$	96.9	0.9	N	152.0121; 123.0431; 124.0163; 108.0218	Vanillic acid[b]	0.03	2.80	0.66	2.02	0.06	1.70	0.28	2.11
Hydroxycinnamic acids and derivatives								**10.30**	**14.37**	**11.55**	**11.48**	**7.18**	**9.74**	**14.37**	**9.21**
11.20	515.1408	$C_{22}H_{28}O_{14}$	88.4	-0.9	N	353.0881; 191.0560; 179.0346	Caffeoylquinic acid hexoside I	0.01	-	-	-	0.02	-	-	-
11.75	515.1410	$C_{22}H_{28}O_{14}$	92.7	0.2	N	341.0872; 323.0771; 191.0559; 179.0348; 173.0451; 135.0451	Caffeoylquinic acid hexoside II	0.03	-	-	-	0.02	-	-	-
12.21	343.1040	$C_{15}H_{20}O_9$	96.3	-1.6	N	181.0507; 163.0397; 137.0607; 135.0443	Dihydrocaffeic acid hexose	0.60	7.75	8.47	5.06	0.22	5.20	6.08	4.21
12.21	353.0883	$C_{16}H_{18}O_9$	87.3	-0.7	N	191.0560; 179.0349; 135.0448	Caffeoylquinic acid I	0.04	0.11	-	-	0.03	0.10	0.09	-
12.68	515.1409	$C_{22}H_{28}O_{14}$	92.9	-1.0	N	341.0863; 323.0777; 191.0564; 179.0358; 135.0447	Caffeoylquinic acid hexoside III	0.05	0.17	0.10	0.20	0.03	0.19	0.14	0.14
13.30	355.1033	$C_{16}H_{20}O_9$	99.6	0.3	N	193.0506; 178.0272; 149.0608; 134.0371	Ferulic acid hexoside I	-	1.41	0.15	1.90	-	0.65	0.18	0.84
13.69	337.0926	$C_{16}H_{18}O_8$	81.3	0.8	N	191.0557; 173.0454; 163.0399	Coumaroylquinic acid I	0.04	-	-	-	0.01	-	-	-
13.92	353.0892	$C_{16}H_{18}O_9$	93.6	-4.0	N	191.0566; 179.0349	Caffeoylquinic acid II[g] (chlorogenic acid)	0.94	0.79	0.38	1.45	0.68	1.00	1.33	0.74
14.05	325.0926	$C_{15}H_{18}O_8$	93.2	-0.1	N	163.0400; 119.0502	Comaroyl hexoside	0.10	0.32	0.24	0.15	0.02	0.33	0.66	0.12
14.17	353.0892	$C_{16}H_{18}O_9$	84.7	-1.0	N	191.0558; 179.0347; 135.0452	Caffeoylquinic acid III	0.11	0.17	0.04	0.31	0.06	0.14	0.20	0.14
14.73	355.1038	$C_{16}H_{20}O_9$	97.0	-1.5	N	193.0508; 178.0270; 149.0610; 134.0373	Ferulic acid hexoside II	-	0.69	0.39	0.55	-	0.49	0.76	0.75
15.22	353.0887	$C_{16}H_{18}O_9$	95.6	-3.0	N	191.0565	Caffeoylquinic acid IV	0.11	0.18	0.15	0.42	0.11	0.22	0.50	0.39
15.69	337.0932	$C_{16}H_{18}O_8$	99.7	-0.6	N	191.0557	Coumaroylquinic acid II	0.50	-	-	-	0.37	-	-	-
15.85	179.0347	$C_9H_8O_4$	97.0	1.0	N	135.048; 134.0368; 89.0396	Caffeic acid[b]	-	0.40	0.15	0.17	-	0.14	0.14	0.31
15.96	295.0458	$C_{13}H_{12}O_8$	99.2	0.3	N	179.0345; 133.0140; 115.0034	Caffeoylmalic acid	2.37	-	-	-	2.86	-	-	-
16.72	337.0922	$C_{16}H_{18}O_8$	95.9	2.2	N	191.0558	Coumaroylquinic acid	0.15	-	-	-	0.09	-	-	-

							III								
17.25	385.1148	$C_{17}H_{22}O_{10}$	98.7	-2.6	N	267.0703; 249.0592; 223.0378; 205.0353; 147.0302; 113.0244; 91.0556; 85.0296	Sinapic acid hexoside	0.18	1.42	0.98	0.55	0.18	0.76	0.49	0.92
18.02	279.0506	$C_{13}H_{12}O_7$	98.9	0.1	N	163.0398; 133.0139; 119.0499; 115.0033	Coumaroylmalic acid I	0.33	-	-	-	0.09	-	-	-
18.07	365.0886	$C_{17}H_{18}O_9$	95.4	-2.0	N	203.0349; 159.0452; 131.0500; 130.0422; 103.0551	Psoralic acid glucoside	3.62	-	-	-	1.74	-	-	-
18.33	339.0729	$C_{15}H_{16}O_9$	98.1	-2.0	N	309.0621; 223.0610; 208.0375; 193.0137; 164.0478; 149.0242; 133.0143; 115.0038	Sinapic acid malate	0.17	-	-	-	0.18	-	-	-
18.37	279.0506	$C_{13}H_{12}O_7$	99.1	1.1	N	163.0401; 133.0139; 119.0500; 115.0033	Coumaroylmalic acid II	0.09	-	-	-	0.03	-	-	-
18.51	309.0619	$C_{14}H_{14}O_8$	99.6	-0.8	N	193.0505; 178.02687; 149.0602; 133.0144; 115.0033	Ferulic acid malate I	0.69	-	-	-	0.36	-	-	-
18.68	309.0623	$C_{14}H_{14}O_8$	98.0	-2.0	N	193.0502; 134.0371	Ferulic acid malate II	0.18	-	-	-	0.09	-	-	-
19.06	193.0506	$C_{10}H_{10}O_4$	77.6	1.6	N	134.0373	*Trans*-ferulic acid[b]	-	0.61	0.20	0.38	-	0.27	0.07	0.32
19.63	193.0508	$C_{10}H_{10}O_4$	97.3	0.0	N	134.0379	Ferulic acid isomer	-	0.37	0.28	0.34	-	0.25	0.10	0.33
Flavonoids-Flavonols								**20.50**	**21.33**	**38.68**	**3.47**	**21.89**	**27.46**	**53.94**	**2.68**
13.15	771.2010	$C_{33}H_{40}O_{21}$	95.1	-2.5	N/P	609.1470; 463.0889; 462.0810; 301.0359; 300.0281	Quercetin *O*-deoxyhexoside di-hexoside	0.84	1.43	1.53	0.10	0.46	2.87	2.85	0.14
13.30	625.1416	$C_{27}H_{30}O_{17}$	98.9	-0.8	N/P	463.0894; 462.0805, 301.0359	Quercetin *O*-di-hexoside	0.39	0.35	0.36	0.38	0.24	0.59	0.59	0.28
15.53	755.2053	$C_{33}H_{40}O_{20}$	93.2	-1.1	N/P	301.0359; 300.027	Quercetin di-deoxyhexoside hexoside	0.04	0.10	0.04	0.07	0.02	0.11	0.07	0.08
17.14	609.1483	$C_{27}H_{30}O_{16}$	93.1	-3.4	N/P	463.0882; 300.0282; 273.0397; 257.0451; 229.0502; 178.9984; 151.0032; 121.0296; 107.0140	Quercetin 3-*O*-rutinoside[g] (rutin)	14.46	16.34	31.41	0.71	14.96	19.20	43.68	0.75
17.89	463.0883	$C_{21}H_{20}O_{12}$	99.5	-0.3	N/P	301.0349; 300.0272; 151.0034	Quercetin 3-*O*-glucoside[g] (isoquercetin)	4.28	1.95	2.55	1.05	4.67	2.04	3.17	0.86
18.57	549.0893	$C_{24}H_{22}O_{15}$	99.0	-1.2	N/P	505.0987; 463.0874; 301.0354; 300.0279	Quercetin 3-*O*-(6"-malonyl)glucoside	0.49	0.48	1.45	0.30	1.54	1.60	3.00	0.24
23.05	301.0373	$C_{15}H_{10}O_7$	83.2	-0.8	N/P	273.0409; 178.9990; 151.0035; 121.0295; 107.0139	Quercetin[b]	-	0.69	1.34	0.86	-	1.06	0.59	0.33

Flavonoids-Flavones								**26.16**	**17.33**	**18.37**	**8.36**	**28.35**	**8.21**	**17.33**	**7.48**
14.61	579.1361	$C_{26}H_{28}O_{15}$	97.7	-1.0	N/P	561.1247; 519.1140; 489.1039; 459.0930; 429.0827; 399.0721; 369.0616; 285.0389; 133.0289	Luteolin *C*-hexoside *C*-pentoside I	1.09	0.21	0.27	-	0.87	0.21	0.18	-
14.77	579.1361	$C_{26}H_{28}O_{15}$	96.6	-1.0	N/P	561.1251; 519.1139; 489.1045; 459.0942; 429.0833; 399.0733; 369.0619; 285.0389; 133.0297	Luteolin *C*-hexoside *C*-pentoside II	2.05	0.29	0.36	-	1.59	0.32	0.34	-
14.98	563.1410	$C_{26}H_{28}O_{14}$	97.6	-1.1	N/P	545.1302; 503.1196; 473.1089; 443.0984; 383.0770; 353.0668; 325.0707; 297.0753; 117.0347	Apigenin *C*-hexoside *C*-pentoside I	0.75	0.16	0.17	-	0.83	0.07	0.09	-
15.48	563.1429	$C_{26}H_{28}O_{14}$	92.2	-2.2	N/P	545.1307; 503.1199; 473.1098; 443.0980; 383.0780; 353.0673; 325.0715; 297.0769; 117.0344	Apigenin *C*-hexoside *C*-pentoside II	13.79	5.52	6.05	0.50	13.54	1.83	3.21	0.70
15.97	447.0939	$C_{21}H_{20}O_{11}$	97.0	-1.6	N/P	429.0833; 387.0722; 357.0615; 327.0513; 285.0404; 133.0138	Luteolin 6-*C*-glucoside (isoorientin)	0.68	0.87	1.01	0.85	0.45	0.40	0.97	0.35
16.15	563.1429	$C_{26}H_{28}O_{14}$	92.3	-2.2	N/P	545.1303; 503.1186; 473.1098; 443.0982; 383.0776; 353.0670; 297.0767; 117.0357	Apigenin 6-*C*-hexose-8-*C*-pentose III	3.47	1.04	0.89	0.05	3.36	0.22	0.41	0.09
16.52	447.0939	$C_{21}H_{20}O_{11}$	99.3	-0.2	N/P	357.0613; 327.0510; 285.0397; 133.0291	Luteolin 8-*C*-glucoside (orientin)	0.92	0.91	1.20	0.49	1.59	0.71	1.35	0.55
16.83	577.1563	$C_{27}H_{30}O_{14}$	97.6	0.0	N/P	457.1393; 413.0873; 293.0454	Apigenin *C*-hexoside *C*-deoxyhexoside	1.13	1.99	2.57	0.82	1.00	0.54	0.82	0.27
17.45	431.0992	$C_{21}H_{20}O_{10}$	97.7	-1.8	N/P	341.0664; 311.0561; 283.0612; 269.04524; 268.0372; 117.0342	Apigenin 8-*C*-glucoside (vitexin)	1.53	3.29	3.69	1.26	4.21	2.06	2.57	1.91
17.89	447.0950	$C_{21}H_{20}O_{11}$	89.9	-1.0	N/P	285.0406; 284.0334; 197.0817; 175.0250; 133.0277	Luteolin 7-*O*-glucoside[b] (cynaroside)	0.24	0.37	0.36	0.72	0.17	0.19	0.36	0.62
22.46	285.0411	$C_{15}H_{10}O_6$	83.8	-2.1	N/P	267.0306; 257.0470; 243.0301; 241.0516; 217.0511; 213.0562; 197.0618; 175.0400; 151.0038; 133.0294	Luteolin[b]	0.37	0.75	1.07	2.35	0.56	0.76	0.50	1.51

24.27	269.0458	$C_{15}H_{10}O_5$	99.3	-1.2	N/P	241.0492; 227.0351; 225.0539; 201.0556; 183.0441; 181.0650; 159.0455; 151.0035; 149.0245; 117.0348; 107.0139	Apigenin[b]	0.14	1.94	0.74	1.32	0.18	0.90	0.89	1.48
Flavonoids-Flavanones								**0.07**	**5.35**	**10.25**	**1.90**	**0.06**	**2.14**	**3.62**	**2.04**
16.13	611.1632	$C_{27}H_{32}O_{16}$	89.2	-2.4	N	449.1090; 287.0571; 151.0037; 135.0445	Eriodictyol di-hexoside	-	0.75	1.04	0.11	-	0.18	0.36	0.23
17.95	449.1094	$C_{21}H_{22}O_{11}$	95.9	-1.3	N	287.0556; 151.0036; 135.0450; 107.0142	Eriodictyol hexoside I	-	0.98	3.09	0.18	-	0.26	1.45	0.41
19.93	449.1093	$C_{21}H_{22}O_{11}$	98.7	-1.0	N	287.0553; 151.0032; 135.0450; 107.0138	Eriodictyol hexoside II	-	0.57	0.99	0.29	-	0.27	0.22	0.23
22.85	287.0564	$C_{15}H_{12}O_6$	99.6	-1.0	N	151.0030; 135.0448; 125.0241; 107.0136; 83.0135	Eriodictyol	-	1.46	3.41	0.70	-	0.73	0.81	0.38
24.58	271.0611	$C_{15}H_{12}O_5$	99.2	-0.1	N	177.0194; 151.0030; 119.0503; 107.0138	Naringenin	0.07	1.60	1.72	0.61	0.06	0.71	0.78	0.79
Flavonoids-Flavanols								**0.03**	**0.20**	**0.06**	**0.72**	**0.04**	**0.17**	**0.20**	**0.27**
14.61	289.0720	$C_{15}H_{14}O_6$	99.3	-0.7	N	245.0797; 205.0512; 203.0709; 161.0615; 125.0238	(+)-catechin[b]	0.03	0.20	0.06	0.72	0.04	0.17	0.07	0.27
Flavonoids-Flavanonols								**-**	**0.42**	**0.66**	**0.79**	**-**	**0.52**	**0.42**	**0.95**
19.50	303.0509	$C_{15}H_{12}O_7$	97.5	0.0	N	285.0385; 151.0033; 125.0243	Dihydroquercetin (taxifolin)	-	0.42	0.66	0.79	-	0.52	0.50	0.95
Flavonoids-Isoflavones								**19.37**	**7.92**	**1.34**	**42.65**	**13.65**	**19.86**	**2.22**	**50.27**
22.71	547.1092	$C_{25}H_{24}O_{14}$	98.7	-0.7	N/P	503.1264; 299.0564; 284.0364; 165.0191; 149.9951; 133.0293; 121.0295	Hydroxygenistein methyl ether malonylhexoside	0.03	-	-	-	0.01	-	-	-
24.38	269.0458	$C_{15}H_{10}O_5$	98.3	-1.2	N/P	241.0468; 225.0558; 201.0558; 151.0041; 133.0284; 119.0504; 117.0343; 107.0137	Genistein[b]	0.14	-	-	-	0.09	-	-	-
25.80	299.0564	$C_{16}H_{12}O_6$	96.6	-1.3	N/P	298.0475; 285.0356; 284.0315; 256.0375; 240.0420; 239.0336; 165.0188; 149.9955; 133.0289; 121.0287	7-methoxy 2'-hydroxy genistein (cajanin)	1.09	0.73	0.20	4.97	0.49	1.40	0.19	1.37
26.51	353.1039	$C_{20}H_{18}O_6$	97.2	-2.3	N/P	325.1074; 298.0472; 283.0604; 219.0655; 175.0397; 133.0658; 133.0290	Prenylhydroxygenistein I	1.32	-	-	-	1.45	-	-	-

27.19	353.1039	$C_{20}H_{18}O_6$	84.2	-2.2	N/P	325.1077; 285.1134; 284.0338; 219.0656; 175.0402; 151.0766; 133.0655; 133.0291	Prenylhydroxygenistein II	0.63	0.27	-	2.75	0.66	0.93	-	2.91
27.61	337.108	$C_{20}H_{18}O_5$	94.8	-2.7	N/P	293.0462; 282.0534; 269.1190; 254.0516; 133.0658; 117.0346	Prenylgenistein I	0.05	0.37	0.04	0.35	0.13	0.46	0.12	1.39
27.62	353.1039	$C_{20}H_{18}O_6$	99.7	-0.4	N/P	325.1080; 285.1134; 284.0329; 219.0663; 175.0395; 151.0760; 151.0032; 133.0658; 133.0294	Prenylhydroxygenistein III	8.73	3.52	0.65	27.12	6.13	11.17	0.71	28.02
27,80	283.0617	$C_{16}H_{12}O_5$	98.1	-1.8	N/P	268.0377; 239.0351; 151.0040; 132.0194; 107.0134	Genistein 4'-methyl ether (biochanin A)	0.50	0.74	0.08	0.24	0.25	0.09	0.14	0.08
28.64	337.1087	$C_{20}H_{18}O_5$	98.8	-1.5	N/P	293.0456; 282.0537; 269.0436; 268.0296; 254.0589; 238.0633; 225.0549; 133.0289	Prenylgenistein II	2.08	1.55	0.21	5.04	1.90	4.94	0.90	13.27
29.10	337.1084	$C_{20}H_{18}O_5$	99.0	-0.3	N/P	293.0455; 282.0533; 269.0444; 268.0370; 253.0501; 254.0574; 238,0634; 133.0292	Prenylgenistein III	4.79	0.75	0.15	2.17	2.54	0.87	0.15	3.23
Hydroxycoumarins								**11.28**	**3.46**	**3.28**	**3.51**	**15.50**	**7.13**	**1.94**	**8.85**
13.11	339.0727	$C_{15}H_{16}O_9$	98.0	-1.9	N	177.0192; 133.0295	Esculetin hexoside I	0.60	0.23	0.19	0.68	0.28	0.49	0.33	0.33
13.80	339.0725	$C_{15}H_{16}O_9$	96.6	-1.1	N	177,0192	Esculetin hexoside II	0.21	-	-	-	0.01	-	-	-
15.69	177.0193	$C_9H_6O_4$	98.4	1.1	N	149.0240; 133.0240; 105.0343	Dihydroxycoumarin I	0.99	0.65	0.39	0.60	1.30	0.41	0.23	0.53
18.26	205.0145	$C_{10}H_6O_5$	91.7	0.1	N	161.0240; 133.0294; 117.0342; 105.0346; 89.0399; 77.0398	6-carboxyl-umbelliferone	0.46	-	-	-	0.93	-	-	-
19.25	161.0247	$C_9H_6O_3$	87.1	-1.7	N	133.0292; 117.0348; 105.0347	7-Hydroxycoumarin[b] (umbelliferone)	1.66	1.54	1.06	0.74	2.05	0.71	0.37	1.03
20.81	177.0194	$C_9H_6O_4$	87.4	-0.3	N	149.0219; 133.0287; 105.0349	Dihydroxycoumarin II	0.11	0.74	1.59	0.34	0.06	0.41	0.30	0.40
22.54	205.0506	$C_{11}H_{10}O_4$	99.6	0.1	N	187.0375; 161.0609; 146.0370; 133.0654; 118.0418; 105.0707	Phellodenol A/hydrated form of 4',5'-dihydropsoralen	3.94	0.29	0.04	0.11	7.05	0.71	0.50	1.40
23.03	235.0619	$C_{12}H_{12}O_5$	96.8	-2.8	N	217.0493; 201.0195; 191.0706; 176.0474; 161.0240; 148.0148;	Murrayacarpin B/di-hydrated form of bergapten	1.51	-	-	-	3.03	0.29	0.20	0.10

						133.0293; 117.0343									
27.95	229.0872	$C_{14}H_{14}O_3$	99.4	-0.7	N/P	213.0551; 185.1162; 146.0371; 130.0424; 118.0426	Prenyl-7-hydroxycoumarin	1.80	-	-	1.05	0.78	4.11	-	5.06
Total area								3.8×10^8	2.0×10^7	3.8×10^7	3.0×10^7	4.6×10^8	2.9×10^7	6.3×10^7	2.3×10^7

[a]Exp, experimental; I, Ionisation mode; SF, 'Soltani' fruits; SL, 'Soltani' leaves; SP, 'Soltani' pulps; SS, 'Soltani' skins; TF, 'Temri' fruits; TL, 'Temri' leaves; TP, 'Temri' pulps; TS, 'Temri' skins; RT, retention time; -, non detected.
[b]Identification confirmed by comparison with standards.

Table 2. Phenolic compounds characterized using the positive ionization mode in the studied parts from *F. carica.*

RT (min)	$[M]^+$/ $[M+H]^+$	Formula	Score	Error (ppm)	I[a]	Main fragments *via* MS/MS	Phenolic compound	Relative abundance (%)							
								TL	**TF**	**TS**	**TP**	**SL**	**SF**	**SS**	**SP**
Anthocyanins and derivatives								**-**	**3.7**	**52.80**	**10.20**	**-**	**70.80**	**99.10**	**50.70**
9.03	595.1664	$C_{27}H_{31}O_{15}$	99.0	-1.0	P	449.1079; 287.0559; 269.0420; 213.0547; 157.0268; 137.0242; 121.0277	Cyanidin rutinoside I	-	-	-	-	-	0.81	0.80	-
10.21	757.2193	$C_{33}H_{41}O_{20}$	98.4	-0.7	P	611.1585; 449.1063; 287.0563; 269.0447; 137.0230	Cyanidin 3-rutinoside-hexose	-	-	-	-	-	1.07	2.25	-
10.39	595.1693	$C_{27}H_{31}O_{15}$	98.9	-1.0	P	449.1073; 287.0558; 269.0447; 213.0527; 137.0235	Cyanidin rutinoside II	-	-	-	-	-	-	3.74	-
11.63	611.1619	$C_{27}H_{31}O_{16}$	97.5	-1.8	P	449.1078; 287.0565; 269.0438; 213.0546; 157.0656; 137.0226; 121.0291	Cyanidin 3,5-diglucoside	-	1.87	19.62	5.19	-	9.71	5.97	24.74
13.00	697.1613	$C_{30}H_{33}O_{19}$	96.3	-1.0	P	N.D.	Cyanidin 3-malonylglucosyl-5-glucoside	-	-	-	-	-	1.04	0.83	1.34
13.06	449.1071	$C_{21}H_{21}O_{11}$	97.3	1.8	P	287.0537; 269.0386; 241.0500; 213.0526; 157.0651; 137.0213; 121.0242	Cyanidin 3-glucoside	-	-	-	-	-	1.70	1.70	2.13
13.31	595.1661	$C_{27}H_{31}O_{15}$	99.5	-0.3	P	449.1073; 287.0547; 269.0463; 213.0545; 157.0638; 137.0229; 121.0282	Cyanidin rutinoside III	-	1.85	33.20	5.02	-	51.98	78.00	22.51
13.86	911.2244	$C_{43}H_{43}O_{22}$	98.2	-0.6	P	603.1127; 571.0875; 477.0812; 435.0709; 287.0555; 157.0277; 137.0223; 121.0247	Dimer of cyanidin rutinoside and petunidin	-	-	-	-	-	2.49	3.01	-
13.99	579.1692	$C_{27}H_{31}O_{14}$	97.0	-1.7	P	433.1084; 271.0544;	Pelargonidin 3-	-	-	-	-	-	2.00	2.83	-

						253.0525; 197.0595; 149.0227; 121.0277; 103.0539	rutinoside								
Furanocoumarins and derivatives								**94.30**	**94.50**	**38.60**	**84.40**	**97.60**	**28.20**	**0.60**	**48.30**
15.85	365.0872	$C_{17}H_{16}O_9$	98.2	-1.5	P	203.0339; 175.0384; 147.0439; 131.0489; 119.0488; 101.0390; 91.0541	Hydroxypsoralen hexoside I	2.65	-	-	-	0.20	-	-	-
16.71	365.0871	$C_{17}H_{16}O_9$	96.9	-1.0	P	203.0336; 175.0389; 147.0440; 131.0395; 119.0485; 91.0539	Hydroxypsoralen hexoside II	0.56	-	-	-	0.03	-	-	-
17.21	205.0511	$C_{11}H_8O_4$	88.2	-3.5	N/P	187.0370; 133.0637; 131.0489; 115.0537; 107.0492; 105.0693; 103.0539	Psoralic acid/dihydro-hydroxypsoralen	2.36	-	-	-	1.52	-	-	-
17.59	247.0972	$C_{14}H_{14}O_4$	97.2	-2.8	P	229.0852; 213.0539; 189.0543; 175.0389; 147.0438; 119.0486; 103.0536	Marmesin isomer I	1.49	4.52	22.27	6.58	0.72	6.26	0.35	10.01
17.64	409.1496	$C_{20}H_{24}O_9$	96.2	-1.0	N/P	247.0962; 229.0862; 213.0545; 185.0602; 175.0389; 147.0348; 119.0487; 91.0543	Marmesinin	0.20	-	-	-	0.07	-	-	-
17.77	235.0609	$C_{12}H_{10}O_5$	90.7	-4.1	P	217.0495; 202.0260; 189.0565; 174.0309; 131.0489; 115.0542	Methoxypsoralen derivative (hydrate)	0.86	-	-	-	0.86	-	-	-
21.61	189.0549	$C_{11}H_8O_3$	84.6	-1.3	N/P	161.0608; 147.0439; 133.0638; 119.0489; 105.0699	4',5'-Dihydropsoralen	0.36	-	-	-	0.62	-	-	-
22.05	247.0972	$C_{14}H_{14}O_4$	97.7	-2.9	P	229.0865; 213.0531; 189.0576; 175.0385; 147.0443; 119.0481; 103.0539	Marmesin isomer II[c]	0.87	3.96	6.62	3.82	1.10	8.68	0.14	8.68
22.23	305.1032	$C_{16}H_{16}O_6$	94.3	-3.7	N/P	203.0338; 175.0391; 159.0439; 147.0438; 131.0489; 119.0486; 91.0543	Oxypeucedanin hydrate	1.19	-	-	-	15.94	-	-	-
22.46	203.0340	$C_{11}H_6O_4$	86.2	0.3	N/P	147.0438; 131.0493; 129,0308; 119.0485;	Hydroxypsoralen	1.09	-	-	-	0.54	-	-	-

						101,0388; 91.0541								
24.54	187.0389	$C_{11}H_6O_3$	98.9	0.2	P	159.0435; 131.0487; 115.0536; 103.0537	Psoralen	26.08	48.47	5.99	5.96	29.45	6.79	0.06	3.31
26.08	217.0506	$C_{12}H_8O_4$	94.5	-4.8	P	202.0264; 174.0316; 146.0363; 131.0498; 118.0416; 90.0464; 89.0391	Methoxypsoralen	33.55	37.58	3.68	4.91	36.67	6.51	0.09	3.84
26.20	287.0918	$C_{16}H_{14}O_5$	99.4	-1.2	P	203.0339; 175.0394; 159.0442; 147.0440; 131.0494; 119.0492; 103.0539	Oxypeucedanin	0.39	-	-	-	0.67	-	-	-
28.24	271.0984	$C_{16}H_{14}O_4$	86.4	-5.6	P	229.0506; 215.0348; 203.0350; 201.0554, 187.0399; 173.0604; 159.0447; 131.0495; 117.0702	Isopentenoxypsoralen	0.37	-	-	-	0.15	-	-	-
31.00	285.1132	$C_{17}H_{16}O_4$	96.4	-3.3	P	202.0257; 174.0317; 159.0440; 146.0359; 131.0490; 118.0413	Prenyl methoxypsoralen	22.26	-	-	63.17	9.07	-	-	22.50
Others															
30.85	299.0906	$C_{17}H_{14}O_5$	96.5	2.9	P	284.0691; 267.0664; 256.0742; 243.1029; 166.0271; 137.0603	Hydroxy-dimethoxyisoflavone	5.72	1.80	8.61	5.36	2.40	1.00	0.22	0.95
Total area								1.2×10^8	2.2×10^6	6.3×10^5	3.7×10^6	1.5×10^8	4.2×10^6	3.4×10^7	2.0×10^6

[a]RT, retention time; Exp, experimental; I, ionisation mode; SF, 'Soltani' fruits; SL, 'Soltani' leaves; SP, 'Soltani' pulps; SS, 'Soltani' skins; TF, 'Temri' fruits; TL, 'Temri' leaves; TP, 'Temri' pulps; TS, 'Temri' skins; RT, retention time; -, non detected.

Table 3. Correlation between the antioxidant activity and the total phenolic content (TPC), abundance of the phenolic subfamilies and their main phenolic representatives in the studied fig parts and cultivars. The antioxidant activity was determined by: trolox equivalent antioxidant capacity (TEAC), ferric ion reducing antioxidant power (FRAP) and oxygen radical absorbance capacity (ORAC).

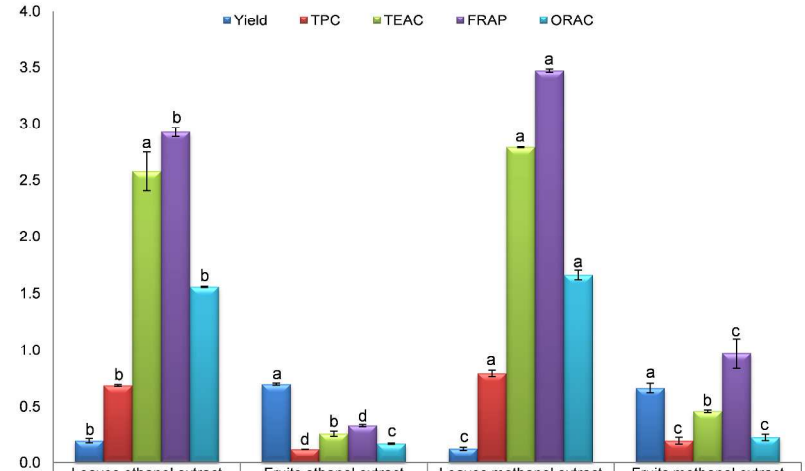
	TEAC	FRAP	ORAC
TPC	0.973**	0.985**	0.974**
TEAC	1	0.974**	0.994**
FRAP	0.974**	1	0.980**
ORAC	0.994**	0.980**	1
Hydroxybenzoic acids[a]	0.980**	0.990**	0.985**
Hydroxycinnamic acids[a]	0.922**	0.968**	0.947**
Flavonols[a]	0.972**	0.984**	0.969**
Flavones[a]	0.981**	0.987**	0.990**
Flavanones[a]	-0.375	-0.351	-0.407
Flavanols[a]	0.435	0.395	0.414
Flavanonols[a]	-0.714**	-0.753**	-0.755**
Isoflavones[a]	0.906**	0.930**	0.935**
Hydroxycoumarins[a]	0.981**	0.972**	0.982**
Anthocyanins[b]	0.832**	0.682*	0.696*
Furanocoumarins[c]	0.976**	0.983**	0.988**
Rutin[a]	0.972**	0.984**	0.969**
Apigenin *C*-hexoside *C*-pentoside II[a]	0.969**	0.987**	0.983**
Prenylhydroxygenistein III[a]	0.889**	0.910**	0.919**
Cyanidin rutinoside III[b]	0.831**	0.688*	0.693*
Psoralen[c]	0.980**	0.982**	0.990**
Methoxypsoralen[c]	0.978**	0.983**	0.989**

* and ** denote a significant correlation at $p < 0.05$ and $p < 0.01$.

[a]Comparison of the abundance in the negative ionization mode of all studied parts.

[b]Comparison of the abundance in the positive ionization mode of the fruit parts.

[c]Comparison of the abundance in the positive ionization mode of all studied parts.



	Leaves ethanol extract	Fruits ethanol extract	Leaves methanol extract	Fruits methanol extract
Yield	0.20	0.70	0.13	0.66
TPC	0.69	0.12	0.79	0.20
TEAC	2.58	0.26	2.79	0.46
FRAP	2.93	0.33	3.47	0.97
ORAC	1.56	0.17	1.66	0.23

Figure 1. Comparison of the yield (g/g), total phenol content (TPC) (g of gallic acid/100 g of sample) and antioxidant activity of leaves and fruits from F. carica cultivar 'Temri' extracted with two different protocols (see the experimental section). The antioxidant activity was evaluated by: trolox equivalent antioxidant capacity (TEAC) (mmol equivalents of Trolox/100 g of sample), ferric ion reducing antioxidant power (FRAP) (mmol equivalents of Fe2+/100 g of sample) and oxygen radical absorbance capacity (ORAC) (mmol equivalents of Trolox/100 g of sample). Data are given as mean ± standard deviation. For each of the studied parameters, values with different letters are significantly different at $p < 0.05$.
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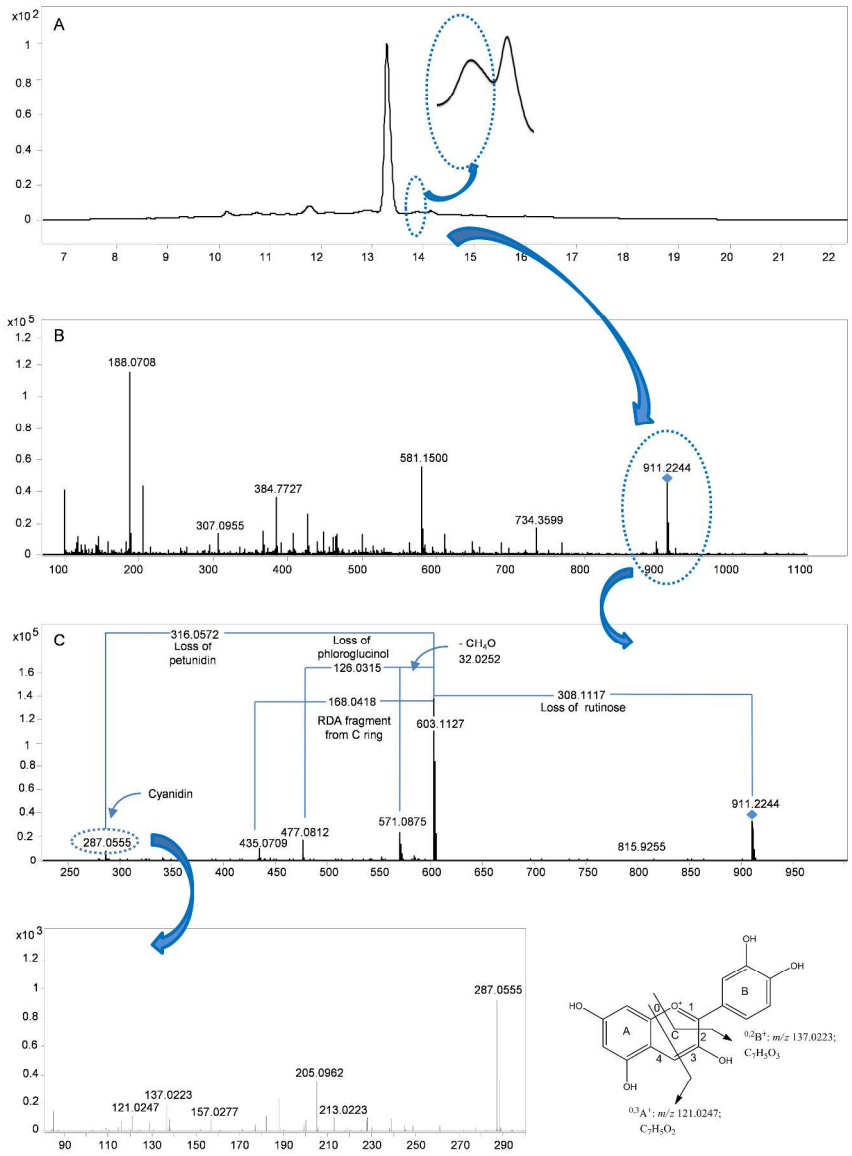

Figure 2. (A) UV chromatograms at 520 nm of 'Soltani' skins, (B) MS spectra for this region highlighting the m/z value of the dimer of petunidin-cyanidin rutinoside and (C) its main MS/MS fragments.
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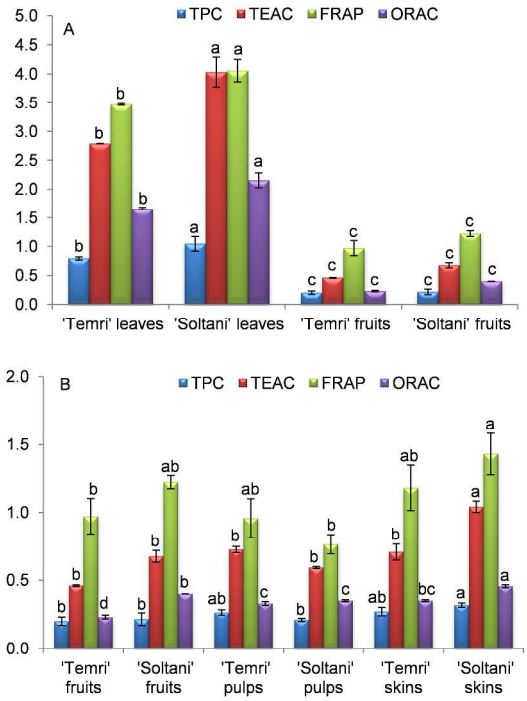

Figure 3. Bar graph representing the total phenol content (TPC) (mg of gallic acid/100 g of sample) and antioxidant activity of (A) leaves and whole fruits, and (B) whole fruits, skins and pulps from F. carica cultivars 'Temri' and 'Soltani'. The antioxidant activity was evaluated by: trolox equivalent antioxidant capacity (TEAC) (mmol equivalents of Trolox/100 g of sample), ferric ion reducing antioxidant power (FRAP) (mmol equivalents of Fe2+/100 g of sample) and oxygen radical absorbance capacity (ORAC) (mmol equivalents of Trolox/100 g of sample) assays. Data are given as mean ± standard deviation. For each of the studied parameters, values with different letters are significantly different at $p < 0.05$.
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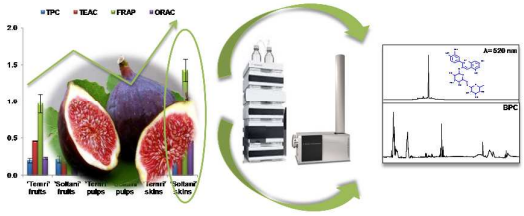

The qualitative and quantitative phenolic composition explains the differences in the antioxidant activity of fig leaves, fruits, pulps, and skins.