Phenolic profile and antioxidant properties of commercial and wild *Fragaria vesca* L. roots: A comparison between hydromethanolic and aqueous extracts

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Running title: Phenolic profile and antioxidant properties of *Fragaria vesca* L. roots

Abstract

The phenolic profile of hydromethanolic extracts, infusions and decoctions of commercial and wild samples of *Fragaria vesca* (wild strawberry) roots was obtained by HPLC-DAD/ESI-MS, and further correlated with their antioxidant properties. Commercial and wild samples showed similarities in terms of flavan-3-ols (TF3O), with catechin derivatives, mainly procyanidins, as major compounds in both samples. The commercial sample presented ellagic acid glycosides, whereas the wild sample presented flavonols (TF) and dihydroflavonols (TdhF, taxifolin derivatives). The infusion of wild sample gave the highest content of total phenolic compounds (TPC), DPPH (2,2-Diphenyl-1-picrylhydrazyl) scavenging activity, reducing power and TBARS (thiobarbituric acid reactive substances) inhibition. The antioxidant capacity (mainly β-carotene bleaching and TBARS inhibition) observed for the wild sample is correlated with TF3O, TF and TPC. Overall, the high antioxidant potential of *F. vesca* roots was demonstrated and could be achieved directly by consumption of infusions/decoctions or by incorporating hydromethanolic extracts in antioxidant formulations.

Keywords: *Fragaria vesca* L.; commercial/wild; alcoholic/aqueous extracts; phenolic compounds; antioxidant activity.

1. Introduction

With the increasing aging of the world's population and simultaneously the lifestyle that society has today, the occurrence of oxidative stress in cells, and consequently, the production of reactive species of oxygen (ROS) is also increasing, which has been related with a higher incidence of cardiovascular, brain and immune system diseases (Carocho and Ferreira, 2013). To prevent, delay or stop this process, antioxidants obtained from herbs may act as reducing agents, free radical scavengers or singlet oxygen quenchers. Through synergistic and additive effects of those bioactive compounds, natural extracts can provide higher beneficial effects when compared to individual molecules (Liu, 2003).

Fragaria vesca L., wild strawberry, belongs to Rosaceae family and is commonly found in forests, slopes and roadsides. Widely spread across Europe, it can also be found in Korea, Japan, North America and Canada (Castroviejo et al., 1998). The roots of wild strawberry are traditionally used to prepare decoctions and infusions for cough symptoms, urinary tract infections, haemorrhoids, diarrhoea, and gout. These preparations also show diuretic properties, anti-dysenteric and antiseptic capacity, functioning as detoxifier, emollient and dermatologic protector (Camejo-Rodrigues et al., 2003; Neves et al., 2009; Özüdogru et al., 2011; Savo et al., 2011).

The bioactive properties related to the fruits, leaves and also roots of strawberry are mainly due to the composition in phenolic compounds, including anthocyanins, proanthocyanidins, flavonols, and derivatives of hydroxycinnamic and ellagic acids (Simirgiotis and Schmeda-Hirschmann, 2010; Sun et al., 2014). Ellagic acid, one of the bases of hydrolysable tannins, is very interesting because it can mostly be found in some berries and nuts. Normally, it is present as ellagitannins or esterified with glucose, while the free form of this compound is rarely found (Clifford and Scalbert, 2000; Pinto et al., 2008). Proanthocyanidins, condensed tannins, can be also found in high concentrations in berries, although they are usually underestimated due to the difficulties associated with extraction, separation and analysis methodologies (Aaby et al., 2012).

There are many reports on the phenolic compounds of *Fragaria x ananassa* variety (Aaby et al., 2012; Andersen et al., 2004; Bodelón et al., 2010; Bordonaba et al., 2011; Fossen et al., 2004; Holzwarth et al., 2012; Lopes da Silva et al., 2007; Pinto et al., 2008; Tarola et al., 2013; Theocharis and Andlauer, 2013), but only a few studies are available regarding phenolic composition of *F. vesca* fruits (Bubba et al., 2012; Gasperotti et al., 2013; Sun et al., 2014; Zheng et al., 2007).

The antioxidant properties of *F. vesca* fruits, leaves (Nuñez-Mancilla et al., 2013; Raudonis et al., 2012), pulp (Özşen and Erge, 2013), achenes and thalamus (Cheel et al., 2007), and of fruits, leaves and roots of *F. chiloensis* (Simirgiotis and Schmeda-Hirschmann, 2010) were also described. However, as far as we know, there are no reports on the phenolic profile and antioxidant activity of *F. vesca* roots. Therefore, in the present study, commercial and wild samples of this material were submitted to different extraction procedures in order to compare their antioxidant potential. Infusions and decoctions were prepared due to their common consumption, while hydromethanolic extracts (the most common procedure to obtain phenolic compounds enriched extracts) could be incorporated in bioactive formulations.

2. Materials and methods

2.1. Samples

The commercial samples of *Fragaria vesca* L. roots were purchased in a local supermarket, while the wild samples were collected in Serra da Nogueira, Bragança, North-eastern Portugal, in July 2013. Voucher specimens (nº 9687) are deposited in the School of Agriculture Herbarium (BRESA). All the samples were lyophilized (FreeZone 4.5, Labconco, Kansas, USA), reduced to a fine dried powder (20 mesh) and mixed to obtain homogenate samples.

2.2. Standards and Reagents

HPLC-grade acetonitrile was obtained from Merck KgaA (Darmstadt, Germany). Formic acid was purchased from Prolabo (WWR International, France). Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) was purchased from Sigma (St. Louis, MO, USA). Phenolic standards were from Extrasynthèse (Genay, France). 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was obtained from Alfa Aesar (Ward Hill, MA, USA). Water was treated in a Milli-Q water purification system (TGI Pure Water Systems, Greenville, SC, USA).

2.3. Preparation of the extracts

Hydromethanolic extraction was performed stirring the sample (1 g) with 30 mL of methanol:water (80:20, *v/v*) at 25 ºC and 150 rpm for 1 h and filtered through Whatman No. 4 paper. The residue was then extracted with one additional 30 mL portion of the hydroalcoholic mixture. The combined extracts were evaporated at 35 ºC under reduced pressure (rotary evaporator Büchi R-210, Flawil, Switzerland) and then further lyophilized (FreeZone 4.5, Labconco, Kansas City, MO, USA).

For infusion preparation the sample (1 g) was added to 200 mL of boiling distilled water and left to stand at room temperature for 5 min, and then filtered under reduced pressure. For decoction preparation the sample (1 g) was added to 200 mL of distilled water, heated (heating plate, VELP scientific) and boiled for 5 min. The mixture was left to stand for 5 min and then filtered under reduced pressure. The obtained infusions and decoctions were frozen and lyophilized.

2.4. Phenolic profile

Phenolic compounds were determined by HPLC (Hewlett-Packard 1100, Agilent Technologies, Santa Clara, USA), as previously described by the authors (Santos et al., 2013). Double online detection was carried out in the diode array detector (DAD) using 280 nm and 370 nm as preferred wavelengths and in a mass spectrometer (API 3200 Qtrap, Applied Biosystems, Darmstadt, Germany) connected to the HPLC system via the DAD cell outlet. The phenolic

compounds were identified by comparing their retention time, UV-vis and mass spectra with those obtained from standard compounds, when available. Otherwise, peaks were tentatively identified comparing the obtained information with available data reported in the literature. For quantitative analysis, a calibration curve for each available phenolic standard was constructed based on the UV signal: catechin (y=158.42x+11.38, R^2=0.999); ellagic acid (y=32.748x+77.8, R^2=0.999); epicatechin (y=129.11x+11.663, R^2=0.9999); quercetin-3-*O*-glucoside (y=253.52x-11.615, R^2=0.999); isorahmetin-3-*O*-rutinoside (y=327.42x+313.78, R^2=0.999) and taxifolin (y=478.06x+657.33, R^2=0.999). For the identified phenolic compounds for which a commercial standard was not available, the quantification was performed through the calibration curve of other compound from the same phenolic group. The results were expressed in mg per g of hydromethanolic extract or lyophilized infusion and decoction.

2.5. Antioxidant activity evaluation

The lyophilized hydromethanolic extracts, infusions and decoctions were re-dissolved in methanol:water (80:20, *v/v*) and water, respectively, to obtain stock solutions of 2.5 mg/mL. These solutions were further diluted to different concentrations to be submitted to the following assays. DPPH radical-scavenging activity was evaluated by using an ELX800 microplate reader (Bio-Tek Instruments, Inc; Winooski, USA), and calculated as a percentage of DPPH discolouration using the formula: $[(A_{DPPH}-A_S)/A_{DPPH}] \times 100$, where A_S is the absorbance of the solution containing the sample at 515 nm, and A_{DPPH} is the absorbance of the DPPH solution. Reducing power was evaluated by the capacity to convert Fe^{3+} into Fe^{2+}, measuring the absorbance at 690 nm in the microplate reader mentioned above. Inhibition of β-carotene bleaching was evaluated though the β-carotene/linoleate assay; the neutralization of linoleate free radicals avoids β-carotene bleaching, which is measured by the formula: β-carotene absorbance after 2h of assay/initial absorbance) × 100. Lipid peroxidation inhibition in porcine (*Sus scrofa*) brain homogenates was evaluated by the decreasing in thiobarbituric acid reactive

substances (TBARS); the colour intensity of the malondialdehyde-thiobarbituric acid (MDA-TBA) was measured by its absorbance at 532 nm; the inhibition ratio (%) was calculated using the following formula: [(A - B)/A] × 100%, where A and B were the absorbance of the control and the sample solution, respectively (Santos et al., 2013). The final results were expressed in EC_{50} values (μg/mL), sample concentration providing 50% of antioxidant activity or 0.5 of absorbance in the reducing power assay. Trolox was used as positive control.

2.6. Statistical analysis

For each plant material, three samples were used and all the assays were carried out in triplicate. The results are expressed as mean values and standard deviation (SD). The results were analyzed using one-way analysis of variance (ANOVA) followed by Tukey's HSD Test with $\alpha = 0.05$. This treatment was carried out using SPSS v. 20.0 program.

3. Results and Discussion

3.1 Phenolic profile

Exemplificative phenolic profile of the hydromethanolic extract prepared from commercial and wild samples of *F. vesca* are shown in **Figure 1** and **2**. Peak characteristics (retention time, λ_{max} in the visible region, mass spectral data) and tentative identifications are presented in **Table 1**, whereas the quantification of both samples (hydromethanolic extracts, infusions and decoctions) is given in **Table 2**. Thirty-four phenolic compounds were identified, seventeen flavan-3-ols (*i.e.*, catechins and proanthocyanidins), ten ellagic acid/HHDP derivatives, three flavonols (*i.e.*, isorhamnetin and quercetin derivatives) and four dihydroflavonols (*i.e.*, dihydroquercetin derivatives).

3.1.1 Flavan-3-ols

Peaks 1, 3-17 and 19 were tentatively identified as flavan-3-ol derivatives according to their UV spectra and pseudomolecular ions. Peaks 6 and 11 were positively identified as (+)-catechin and (-)-epicatechin, respectively, according to their retention time, mass and UV-vis characteristics by comparison with commercial standards. Peak 6 was the major phenolic compound found in the wild sample of *F. vesca*. Peak 1 presented a pseudomolecular ion $[M-H]^-$ at *m/z* 451, releasing an MS^2 fragment at *m/z* 289 ($[M-H-162]^-$, loss of a hexosyl moiety), corresponding to a catechin monomer. This compound was tentatively identified as (epi)catechin hexoside, identity that was coherent with its earlier elution (higher polarity) compared with the parent aglycones (Peaks 6 and 11).

Proanthocyanidins (PAC) were assigned based on their pseudomolecular ions and MS^2 fragmentation patterns, characterised by the formation of product ions from the cleavage of the interflavan bond and retro-Diels-Alder (RDA) and heterocyclic ring fissions (HRF) of the elementary flavan-3-ol units (Friedrich et al., 2000; Gu et al., 2003). As for the cleavage of the interflavan bond, it has been reported that the terminal (lower) units of the PAC oligomer are released intact, while the extension (upper) units suffer a structural rearrangement yielding ions 2 Da lower than the original flavanol constituents (Friedrich et al., 2000; Gu et al., 2003). The analysis of the produced fragments provides information about the type elementary units and might also inform about their relative position in the PAC oligomer. Mass spectra do not allow, however, establishing the position of the linkage between flavanol units (*i.e.*, C4-C8 or C4-C6) nor differentiating between isomeric catechins (*e.g.*, catechin/epicatechin or afzelechin/epiafzelechin).

Peaks 3, 4 and 16 presented the same pseudomolecular ion $[M-H]^-$ at *m/z* 577 and MS^2 fragmentation patterns coherent with B-type (epi)catechin dimers (*i.e.*, (epi)catechin units with C4–C8 or C4–C6 interflavan linkages). Characteristic product ions were observed at *m/z* 451 (-126 mu), 425 (-152 mu) and 407 (-152-18 mu), attributable to the HRF, RDA and further loss of water from an (epi)catechin unit, and at *m/z* 289 and 287, that could be associated to the

fragments corresponding to the lower and upper (epi)catechin unit, respectively. In the case of these three compounds comparison of their retention times with standards available in the laboratory allowed their tentative identification as the procyanidin dimers B3 (catechin-4,8-catechin), B1 (epicatechin-4,8-catechin) and B2 (epicatechin-4,8-epicatechin), respectively (Du et al., 2013; Pekic et al., 1998). Similarly, peaks 5, 9, 13 and 19 (pseudomolecular ions $[M-H]^-$ at *m/z* 865) and peaks 7 and 14 (pseudomolecular ions $[M-H]^-$ at *m/z* 1153) can be assigned as B-type (epi)catechin trimers and tetramers, respectively. In all cases, fragmentation patterns are coherent with those expected for such types of compounds, *i.e.*, similar at those observed for PAC dimers but with additional fragments from the alternative cleavages of different interflavan bonds. The same type of compounds have also been found and described in wild roots of *F. chiloensis* (Simirgiotis and Schmeda-Hirschmann, 2010) and fruits of *F. vesca* (Bubba et al., 2012; Sun et al., 2014).

Peak 10 showed an $[M-H]^-$ at *m/z* 561, consistent with the presence of an (epi)afzelechin and an (epi)catechin units. MS^2 fragments at *m/z* 435 and 407 can be ascribed to HRF and RDA cleavages of the (epi)catechin unit, whereas the observation of the ion at *m/z* 289 would suggest that this latter would be located in terminal position, so that the compound could be assigned as the dimeric properlagonidin (epi)afzelechin-(epi)catechin. The presence of a similar dimer in *F. vesca* berries was reported by Bubba et al. (2012).

Peaks 8, 12 and 17 showed an $[M-H]^-$ at *m/z* 849, consistent with the presence of one (epi)afzelechin and two (epi)catechin units. In all cases, no fragment at *m/z* 273 corresponding to the (epi)afzelechin unit was observed indicating that it was not located in terminal position. Similarly, the presence of that unit in middle position of the trimers must be also discarded owing to the production of the fragment at *m/z* 577 (-272 mu) from the loss of an (epi)afzelechin unit, indicating its position on the end of the structure. The fragment at *m/z* 559 would correspond to the (epi)afzelechin-(epi)catechin dimer produced after the loss of the terminal (epi)catechin unit, whereas this latter was observed as the ion at *m/z* 289. These compounds

could be thus identified as B-type trimers consisting of (epi)afzelechin-(epi)catechin-(epi)catechin; the existence of different compounds can be explained by the presence of different catechin/afzelechin isomers and/or distinct interflavan linkages (C4-C8 or C4-C6). Similar propelargonidin trimers were also reported in fruits of *F. vesca* by Bubba et al. (2012) and Sun et al. (2014).

Peak 15 showed a pseudomolecular ion $[M-H]^-$ at *m/z* 833, coherent with two (epi)afzelechin and one (epi)catechin units. Product ions were observed at *m/z* 561 (-272 mu, loss of an (epi)afzelechin unit), 543 (-272-18 mu, further loss of water), 407 (-272-154 mu, loss of an (epi)afzelechin unit + RDA cleavage of the (epi)catechin unit) and 289 (-272-272 mu, loss of two (epi)afzelechin units; terminal (epi)catechin unit), which identifying the peak as a B-type (epi)afzelechin-(epi)afzelechin-(epi)catechin trimer, also reported by Bubba et al. (2012).

Overall, the wild sample (mainly the infusion) showed higher contents of total flavan-3-ols in comparison with the commercial sample, mainly due to the presence of the compound (+)-catechin (peak 6; 65.07 mg/g). However in the commercial sample it was the decoction that presented the highest concentration of this type of compounds, due to the presence of the B-type (epi)catechin trimer (peak 5; 7.56 mg/g). Simirgiotis and Schmeda-Hirschmann (2010) described a similar flavan-3-ol profile in wild roots of *F. chiloensis*, mainly consisting of trimers and tetramers of (epi)catechin; however, the quantification of the individual compounds was not presented, so it cannot be compared.

3.1.2. Ellagic acid derivatives

These compounds were only quantifiable in the commercial sample of *F. vesca*; the wild sample only presented traces of these derivatives. Therefore, it can be concluded that the profile in ellagic acid derivatives is not specific of a plant species, depending on the cultivar and environmental factors with influence on the secondary metabolism.

Peak 2 presented an $[M-H]^-$ ion at *m/z* 633, presenting MS^2 fragment ions at *m/z* 481 (loss of a galloyl moiety, 152 mu), *m/z* 463 (loss of gallic acid, 170 mu) and *m/z* 301 ($[M-H-302]^-$), which is an evidence of the presence of an HHDP group in the molecule. A compound with similar characteristics was reported in *F. vesca* berries by Bubba et al. (2012) and in strawberry fruits by Gasperotti et al. (2013) that identified it as strictinin (i.e., galloyl-HHDP-glucose).

Peaks 18 and 21 were identified as bis-galloyl-HHDP-glucose isomers, presenting a pseudomolecular ion at *m/z* 935, with the main fragmentation ions at *m/z* 633 and *m/z* 301, corresponding to the loss of one HHDP unit and a galloyl-hexose unit, respectively. Similar compounds were reported in *F. vesca* fruits (Bubba et al., 2012; Sun et al., 2014) and identified as casuarictin/potentillin isomers. Peak 22 presented a pseudomolecular ion $[M-H]^-$ at *m/z* 933 and fragment ions at *m/z* 915, 631, 451 and 301, in agreement with those attributed to castalagin or vescalagin isomers, previously reported in *F. vesca* (Bubba et al., 2012; Gasperotti et al., 2014). Peaks 20 and 25 were identified as sanguiin H-10 isomers, also reported in *F. vesca* by Bubba et al. (2012), presenting $[M-H]^-$ at *m/z* 1567 which produced a sequence of fragments, *m/z* 935 (loss of galloyl diHHDP glucose structure) followed by the characteristic fragments *m/z* 633 and 301. Peak 25 was the major ellagic acid derivative found in the hydromethanolic and aqueous extracts of the commercial sample.

Even though the above compounds (2, 18, 21, 22, 20 and 25) were previously reported in fruits of *F. vesca* (Bubba et al., 2012; Sun et al., 2013; Gasperotti et al., 2014), as well as in leaves and fruits of *F. chiloensis* (Simirgiotis and Schmeda-Hirschmann, 2010), this is the first time that they are described in roots of *F. vesca*.

Peaks 27, 29, 31 and 34 were assigned as ellagic acid derivatives, due to their UV-vis and mass spectra characteristics. Peak 31 was positively identified as ellagic acid, according to its retention, mass and UV-vis characteristics by comparison with commercial standard. Peak 27 and 29 presented a pseudomolecular ion $[M-H]^-$ at *m/z* 447. Various compounds with similar UV and mass spectral characteristics were found in fruits of *F. vesca* (Bubba et al., 2012; Sun et al.,

2014), strawberry (Gasperotti et al., 2013) and fruits and leaves of *F. chiloensis* (Simirgiotis and Schmeda-Hirschmann, 2010), and identified either as methylellagic acid pentosides or ellagic acid rhamnoside. In our case, the production of only one MS^2 fragment ion at *m/z* 301 (-146 mu, loss deoxyhexosyl moiety), corresponding to ellagic acid, suggested that they might be ellagic acid deoxyhexosides rather than methylellagic acid pentosides. Peak 34 possessed a molecular weight 15 mu higher than peaks 27 and 29, suggesting the presence of an additional methyl group. A similar compound was positively identified in *F. vesca* fruits based on mass, NMR and CD analyses by Gasperotti et al. (2013) as 3-*O*-methyl ellagic acid 3'-*O*-rhamnoside. To our knowledge this is the first time that these ellagic acid derivatives are described in *F. vesca* roots.

The distinct extracts of the commercial sample showed significant differences regarding ellagic acid derivatives, with hydromethanolic extracts presenting the highest concentration followed by decoction and infusion (16.06 mg/g, 3.88 mg/g and 2.81 mg/g, respectively).

3.1.3. Flavonols and dihydroflavonols

Peaks 23, 24, 26 and 28, all of them presenting a pseudomolecular ion $[M-H]^-$ at *m/z* 435, were identified as dihydroquercetin pentosides, based upon their UV spectra with λ_{max} at 292 nm and the production of an MS^2 fragment ion at *m/z* 303 (loss of a pentosyl moiety). Peak 28, the second major compound found in the wild sample, was tentatively assigned as taxifolin-3-*O*-arabinofuranoside, as that compound was previously reported as a major component in roots of *Fragaria x ananassa* (Ishimaru et al., 1995) and in fruits of *F. vesca* (Sun et al., 2014).

Peaks 30 and 32 presented UV spectra with λ_{max} around 350 nm and an MS^2 product ion at *m/z* 301 indicating that they corresponded to quercetin derivatives. According to their pseudo molecular ions, they were identified as quercetin-3-*O*-glucoside (peak 30; $[M-H]^-$ at *m/z* 463), which was confirmed by comparison with a commercial standard, and quercetin-*O*-pentoside (peak 32; $[M-H]^-$ at *m/z* 433). Finally, peak 33 presented a pseudomolecular ion $[M-H]^-$ at *m/z* 477 yielding a unique MS^2 fragment ion at *m/z* 315 (-162 mu; isorhamnetin), which was coherent

with an isorhamnetin *O*-hexoside. The presence of quercetin-3-*O*-glucoside has been previously reported in *F. vesca* fruits (Sun et al., 2014), whereas a quercetin pentoside was described in roots of wild *F. chilloensis* (Simirgiotis and Schmeda-Hirschmann, 2010), however nothing was reported about *F. vesca* roots.

Contrary to proanthocyanidins and ellagic acid derivatives, flavonols and dihydroflavonols were only found in the wild sample. In fact, dihydroflavonols represented the second largest family of phenolic compounds found in the wild sample herein analysed, being at higher concentration in the decoction (32.39 mg/g) than in the infusion and the hydromethanolic extract (26.22 mg/g and 13.14 mg/g, respectively). Flavanols were also present in higher concentration in the decoction (0.58 mg/g) of the wild sample, followed by hydromethanolic and infusion extracts (0.53 mg/g and 0.50 mg/g, respectively). The fact that decoction extracts were the ones with the highest concentration of flavonols and dihydroflavonols could be due to the fact that high temperatures improve the efficiency of the extraction by increasing the solubility and diffusion coefficients of the compounds through the cell (Santos-Buelga et al., 2012). These types of compounds were also reported in roots of wild *F. chiloensis* (Simirgiotis and Schmeda-Hirschmann, 2010). The content of total flavonoids determined by those authors (0.55 g quercetin equivalents/100 g dw) was similar to the one presented in the commercial sample of *F. vesca* roots studied herein, although lower than that found in the wild sample.

3.2. Antioxidant activity

Data regarding antioxidant activity of the hydromethanolic extracts, infusions and decoctions obtained from commercial and wild samples of *F. vesca* roots are presented in **Table 3**. In general, wild samples gave lower EC_{50} values (higher antioxidant activity) than commercial samples. The exceptions were for β-carotene bleaching inhibition and TBARS assay, in which the hydromethanolic extracts and infusion (β-carotene bleaching) of commercial sample displayed the lowest EC_{50} value. In the commercial sample, the aqueous extracts gave the highest

DPPH scavenging activity and reducing power (decoctions); and β-carotene bleaching inhibition (infusions). For TBARS assay, it was the hydromethanolic extract that presented the highest antioxidant activity (EC_{50}=6.69 μg/mL). In the wild sample, the aqueous extracts showed higher β-carotene bleaching and TBARS inhibition, while the hydromethanolic extract gave the highest reducing power (EC_{50}=40.98 μg/mL). For DPPH scavenging activity there were no significant differences between the hydromethanolic and aqueous extracts obtained from the wild sample.

The results obtained are similar to the ones described for the methanolic extracts of wild *F. chiloensis* ssp. *chiloensis* f. *chiloensis* roots (EC_{50} DPPH scavenging activity = 64.8 μg/mL; Simirgiotis and Schmeda-Hirschmann, 2010). However, Žugic et al. (2014) reported a lower EC_{50} value for DPPH scavenging activity of methanolic extracts of wild *F. vesca* leaves (13.46 μg/mL).

Correlations of total flavan-3-ols (TF3O), total flavonols and total dihydroflavonols (TF and TdhF, respectively; wild sample), total ellagic acid derivatives (TED; commercial sample) and total phenolic compounds (TPC), with the EC_{50} values obtained in the four antioxidant activity assays were performed. The wild sample showed high and positive correlation between TF3O, TdhF and TPC and β-carotene bleaching inhibition (R^2=0.7955, 0.7432 and 0.8537, respectively) and TBARS inhibition (R^2=0.8466, 0.876 and 0.9253, respectively). It also showed a high correlation between TdhF and reducing power assay (R^2=0.908). For the commercial sample, TF3O showed a high correlation with DPPH scavenging activity, β-carotene bleaching inhibition and TBARS inhibition (R^2=0.5451, 0.6856 and 0.7358, respectively). The fact that in the commercial sample TF3O correlated with DPPH assay might be related to the presence of B-type procyanidin (peaks 9 and 13) and propelargonidin trimers (peak 17), that were not present in the wild sample. Also in the commercial sample, TED showed a high and positive correlation with reducing power (R^2=0.9754), while TPC correlated with DPPH scavenging activity, reducing power and TBARS inhibition (R^2= 0.8676, 0.8176 and 0.5924, respectively). Low

correlations for TED could be explained with the low concentration of these compounds in the commercial sample, when compared to the TPC contents.

Overall, the phenolic compounds profile of commercial and wild *F. vesca* roots presented some similarity regarding flavan-3-ols, being (epi)catechin derivatives (mainly, procyanidins), the major compounds found in both samples. Nonetheless, it could be observed that the commercial sample presented ellagic acid derivatives (mainly, ellagic acid glycosides), while the wild sample presented flavonols and dihydroflavonols (taxifolin derivatives).

The infusion of the wild sample gave the highest content of total phenolic compounds (253.42 mg/g) mainly due to flavan-3-ols (226.7 mg/g). Its decoction also gave the highest content of total dihydroflavonols (32.97 mg/g). It also showed higher DPPH scavenging activity, reducing power and TBARS inhibition. The high antioxidant capacity of the wild sample could be related to the presence of specific phenolic compounds, since high and positive correlations were obtained between TF3O, TF and TPC and β-carotene bleaching, and TBARS inhibition. The commercial sample showed higher content of total ellagic acid derivatives (mainly, the hydromethanolic extract; 46.21 mg/g) and higher β-carotene bleaching inhibition (mainly, the infusion). Although the roots of *F. vesca* are not widely known and used by the general public, this report shows its great antioxidant potential that could be displayed directly by consumption in infusions/decoctions or included in antioxidant formulations (hydromethanolic extract).

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Conflict of interest

The authors declare that they have no conflict of interest.

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