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Detailed analyses of fresh and dried maqui (*Aristotelia chilensis* (Mol.) Stuntz) berries and juice

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ABSTRACT

In this study, a detailed chemical characterization of nutritionally-relevant, quality-determining constituents in dried and fresh fruits as well as juices of maqui (*Aristotelia chilensis* (Mol.) Stuntz) is provided. A total of 8 glycosylated anthocyanins was characterized in maqui fruits, being composed of differently substituted cyanidin and delphinidin derivatives. During processing into juice, a substantial loss in total anthocyanin contents (TAC) was observed. TAC values were also reduced after drying of maqui berries. Likewise, the browning index (BI) of fresh fruits increased during processing. Being composed of flavonol glycosides and ellagic acids, 17 non-anthocyanin phenolics were characterized in all maqui samples. Besides characterizing phenolic compounds, antioxidant activities, total phenolics, major sugars, non-volatile organic acids, minerals and trace elements were quantitated. Moreover, total lipid contents and the fruits' mainly unsaturated fatty acid profiles are reported. The presented results indicate the high potential of maqui as so far under-utilized but extremely pigment-rich "superfruit".

1. Introduction

During the past decade, the interest in dark-colored berries and their potential health benefits has greatly increased. In particular, their phenolic constituents and assumed health benefits were studied with regard to their outstanding antioxidant activity. The color of many dark blue to red berries is due to the high content of anthocyanins, natural phenolic pigments exerting enormous antioxidant capacities. Most frequently, concomitant amounts of flavonoids, phenolic acids, and further phenolic compounds were observed in many edible berries (Wu, Gu, Prior, & McKay, 2004).

Recently, a still limited number of reports about maqui berries (*Aristotelia chilensis* (Mol.) Stuntz, Elaeocarpaceae) became available. The evergreen shrub or tree thrives in the temperate forests from central to southern Chile as well as western Argentina, where it was mostly considered a weed (Dirnböck, Greimler, Lopez S., & Stuessy, 2003). The plant yields small edible purple-black berries of about 5 mm in diameter with one to six seeds. The berries are extremely rich in anthocyanins, being responsible for their intense blackish color and the major proportion of their antioxidant potential, which is one of the highest among known berry fruits of the entire world (Miranda-Rottmann et al., 2002). Due to its high antioxidant capacity, the consumption of maqui was related to health benefits such as anti-diabetic, anti-inflammatory effects and the prevention of Alzheimer's disease (Céspedes, El-Hafidi, Pavon, & Alarcon, 2008; Fuentealba et al., 2012; Miranda-Rottmann et al., 2002; Rojo et al., 2012; Schreckinger, Wang, Youzef, Lila, & Gonzalez de Mejia, 2010). Consequently, the interest in maqui as a dietary constituent of functional food products has significantly increased (Escribano-Bailón, Alcalde-Eon, Muñoz, Rivas-Gonzalo, & Santos-Buelga, 2006). However, maqui berries were often classified as novel food or rather "*food that has not been used for human consumption to a significant degree in the EU before 15 May 1997*" (Regulation (EC) No. 258/1997). Nevertheless, several reports about the long-standing food use of maqui berries in Europe are available. Its fresh consumption, juice and jam production as well as its use as a natural food colorant, especially for coloring wine since the end of the 19th century, are well documented (Benn Brothers, 1890; Royal Botanic Gardens, Kew, 1890). According to a weekly trade journal (Benn Brothers, 1890), a total of 26,592 kg, 135,026 kg and 431,392 kg of maqui berries for coloring wine were imported to Europe during the three years ending 1887, and, more specifically, 500 kg, 115,000 kg, and 315,774 kg to France. In recent years, hardly any plant gained as much popularity as maqui. Unexpectedly, however,

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detailed reports on the chemical composition of maqui fruit and derived products are scare to date.

The main goal of this study was to demonstrate the high potential of maqui berries and derived products by their detailed chemical characterization. Therefore, fresh fruits were processed into juice and dried in order to compare fresh fruits with juice and dried fruit samples regarding their chemical composition. Besides investigating the genuine profile and process-related changes of the contained anthocyanins, the presented study aimed at a comprehensive phytochemical characterization of maqui berries and derived products, including non-anthocyanin phenolic compounds, antioxidant activities, lipid content, fatty acid profiles, sugars and non-volatile acids.

2. Materials and methods

2.1. Plant material

Fresh maqui berries (*A. chilensis* (Mol.) Stuntz) were collected in the Aysén region nearby Coihaique in Patagonia end of February 2013. Dried fruits were produced from the fresh samples applying microwave-assisted vacuum dry process (pop dry® process: pre-drying in a tray dryer at 80 °C and subsequent microwave-vacuum drying at 75 °C) by Salus Chile (Villarrica, Chile), and ground with a knife mill to obtain a homogenous powder. The fruits were shipped frozen (−20 °C) and stored at −20 °C until further use.

The fruit juice was produced at the pilot plant of the University of Hohenheim by the following process. After thawing at 8 °C, the fruit mash was heated for 2 min at 85 °C to inactivate native enzymes. The mashes were then macerated with 0.05% (v/w) Pectinex Ultra Color (β-glycosidase free according to manufacturer, Novozymes, Denmark) for 1 h at 35 °C and subsequently pressed in a cloth press (Bucher-Guyer, Niederweningen, Switzerland) to separate pomace from juice. The obtained juices were pasteurized for 2 min at 85 °C, cooled again using a tubular heat exchanger (Ruland, Neustadt, Germany), and filled into light protected bottles. The achieved juice yield from the fresh berries was 50.2% (w/w). The juice was stored at -20 °C until further use.

2.2. Solvents and reagents

The following analytical standards were used for qualitative and quantitative HPLC–DAD–ESI/MS^n analyses: cyanidin 3-glucoside, delphinidin 3-glucoside (Extrasynthèse, Genay Cedex, France); myricetin 3-glucoside, neochlorogenic acid (Sigma–Aldrich, St. Louis, MO, USA); isoquercetin, kaempferol 3-glucoside, caffeic acid, *p*-coumaric acid, ferulic acid (Roth, Karlsruhe, Germany); ellagic acid (Serva, Heidelberg, Germany). Folin–Ciocalteu reagent, TPTZ [2,4,6-tripyridyl-s-triazine], trolox [(±)-6-hydroxy-2,5,7,8-tetra-methyl-chroman-2-carboxylic acid], $FeCl_3 \cdot 6H_20$, ABTS [2,2′-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt] and ABAP [2,2′-azo-bis-(2-amidino-propane) dihydrochloride] were supplied by Sigma–Aldrich (St. Louis, MO, USA). All further solvents and reagents were from Merck and VWR (Darmstadt, Germany) and at least of analytical grade. Deionized water was used throughout.

2.3. Extraction of anthocyanins and non-anthocyanin phenolic compounds

Frozen maqui berries were ground with liquid nitrogen prior to extraction. For anthocyanin extraction, fruit samples were brought to room temperature, and aliquots of 20–50 mg were extracted with 4 mL acidified methanol (0.1% HCl, v/v) for 30 s using a probe sonicator (microtip MS 72, amplitude 75%, Sonopuls HD 3100, Bandelin electronics, Berlin, Germany). After centrifugation for 3 min at 2500 rpm, the methanolic phase was separated, and solid residues were re-extracted 3–4 times until being colorless. Supernatants were combined, concentrated to dryness by a gentle nitrogen stream, re-suspended in deionized water, membrane-filtered (0.45 μm), and stored at −80 °C until analyses.

For extraction of non-anthocyanin phenolic compounds, methanolic maqui extracts were extracted with ethyl acetate, while the above-mentioned maqui juice was directly extracted with ethyl acetate without preceding methanolic extraction. If necessary, samples were diluted with deionized water prior to extraction. Subsequently, the pH was adjusted to 1.5 with diluted HCl, and phenolic compounds were separated by a fourfold repeated extraction with ethyl acetate using the above mentioned probe sonicator. The combined extracts were evaporated to dryness by nitrogen gas and re-suspended in methanol. After membrane filtration (0.45 μm), samples were stored at −80 °C until quantitation. Anthocyanin and non-anthocyanin analyses were conducted in triplicate.

2.4. HPLC–DAD and HPLC–DAD–ESI/MS^n-analysis

HPLC analyses were performed with an Agilent 1100 series HPLC system equipped with a G1315B diode array detector (DAD). Anthocyanins were separated using a C18 Atlantis (250 × 4.6 mm i.d., 5 μm) column (Waters, Wexford, Ireland) protected by a C18 security guard column (4 × 3.0 mm i.d., Phenomenex, Torrance, USA) maintained at 25 °C. Elution solvent A for anthocyanin separation consisted of water/methanol/formic acid (77/13/10, v/v/v), while solvent B was a mixture of water/methanol/formic acid (30/60/10, v/v/v). Separation was achieved using an initial solvent composition of 6% (B), increased to 30% (B) within 15 min, and subsequently ramped to 36% (B) within 5 min, increased to 100% (B) in 5 min followed by a 2 min isocratic period, and finally decreased to 6% (B) in 3 min prior to isocratic re-equilibration at 6% (B) for 5 min. Total run time was 35 min at a flow rate of 0.8 mL/min. The injection volume was 5 μL. Anthocyanins were monitored at 520 nm, and additional UV/Vis spectra were recorded in the range of 200–700 nm. Non-anthocyanin phenolics were separated by a previously published method of Gironés-Vilaplana et al. (2012), although a slightly different column with a 3 mm instead of 4.6 mm diameter was used (Luna C18 column, 250 × 3 mm, 5 μm particle size; Phenomenex, Macclesfield, U.K.) and operated at 30 °C with a flow rate of 0.6 mL/min.

The HPLC–DAD was serially interfaced with a multi-stage ion trap mass spectrometer (Esquire 3000 plus, Bruker Daltonics, Bremen, Germany) *via* an atmospheric pressure electrospray ionization (ESI) probe operated in positive and negative ion mode for anthocyanin and non-anthocyanin analyses, respectively. Further MS operating conditions for anthocyanin identification were set according to Sadilova, Stintzing, and Carle (2006). Regarding the characterization of non-anthocyanin phenolics, the mass spectrometric method of Gironés-Vilaplana et al. (2012) was used with identical settings.

Identification of compounds was accomplished by comparison of their retention time, UV/Vis and mass spectral data with those of authentic standards. When reference compounds were unavailable, compounds were tentatively identified by comparing their UV/Vis absorption characteristics and mass spectral behavior to previously published data (Céspedes et al., 2010; Escribano-Bailón et al., 2006; Fischer, Carle, & Kammerer, 2011; Gironés-Vilaplana et al., 2012; Kammerer, Claus, Carle, & Schieber, 2004; Regos, Urbanella, & Treutter, 2009; Ruiz et al., 2010; Schreckinger et al., 2010; Wu et al., 2004).

While quantitative analyses of non-anthocyanin phenolics were not conducted in the present study, quantitation of anthocyanins was executed based on linear calibration curves of authentic standards. A delphinidin 3-glucoside calibration was used for the quantitation of delphinidin derivatives (compounds A1, A2, A4 and A5), whereas the cyanidin 3-glucoside calibration was used for cyanidin derivatives (compounds A3a/A3b, A6 and A7). The estimated concentrations were subsequently multiplied by a respective molecular-weight-correction factor (MWCF) according to Chandra, Rana, and Li (2001). Total anthocyanin contents (TAC) represent the sum of all individual monomeric anthocyanins.

2.5. Total monomeric anthocyanins and polymeric color

Total monomeric anthocyanin content (TMAC) and polymeric color (browning index, BI) of fruit extracts and juices were estimated based on a pH-differential spectrophotometric method and a bleaching reaction with bisulfite reported by Giusti and Wrolstad (2005), respectively. TMAC was expressed as delphinidin-3-glucoside (Dpd-3-glc; molar extinction coefficient ε_M = 29000 L mol^{-1} cm^{-1}) equivalents, while the BI was expressed in percent (Giusti & Wrolstad, 2005).

2.6. Total phenolic content and antioxidant activity

The total phenolic content was expressed as gallic acid equivalents in g/kg for fruits and g/L for juices, respectively, according to the Folin–Ciocalteu assay as described by Singleton, Orthofer, and Lamuela-Raventós (1999). In addition, both the ferric reducing antioxidant power (FRAP) assay according to Benzie and Strain (1996) and the trolox equivalent antioxidant capacity (TEAC) as described by van den Berg, Haenen, van den Berg, and Bast (1999) were conducted in order to determine the antioxidant activity expressed as trolox equivalents in mmol/kg (fruits) and mmol/L (juices). If necessary, samples and calibrations were diluted in deionized water. A Power Wave XS microplate spectrophotometer was used (Biotek Instruments, Bad Friedrichshall, Germany).

2.7. Chemical characterization of lipids, minerals, trace elements, main sugars and non-volatile acids

Total lipid contents and fatty acid patterns were analyzed by GC/EI–MS^n after accelerated solvent extraction (ASE) according to the method of Thurnhofer and Vetter (2005). In addition to fruits and juices, the pomace derived of maqui juice processing was examined. Prior to ASE, samples were freeze-dried. Fatty acid (FA) compositions of the oils obtained by ASE were determined as fatty acid methyl esters (FAME). For preparation of FAME derivatives, an aliquot of 20 mg of oil and 0.5 mL of methanolic KOH (0.5 M) were mixed for 5 min at 80 °C. Subsequently, samples were cooled and combined with 1 mL of methanolic BF_3. After heating at 80 °C for 5 min, samples were cooled to room temperature in an ice bath and mixed with 2 mL of saturated sodium chloride solution and 2 mL of *n*-hexane. Organic phases including the FAMEs were separated for following GC/EI–MS^n analysis.

Analyses of minerals and trace elements were performed by the 'State Institute for Agricultural Chemistry' (Stuttgart, Germany). Samples were freeze-dried and quantitation of Na, K, Ca, Mg, Cu, Fe, Al, Mn, P, S, Si was carried out using ICP–OES. As, Ba, Cd, Co, Cr, Mo, Ni, Sb, Sn, V, Zn, Zr were analyzed by ICP–MS. Chloride and Hg were determined using ion chromatography (IC) and the cold vapor KD-AAS technique, respectively, according to VDLUFA methods 2.2.2.9 and 2.2.2.2.

Determination of sucrose, D-glucose, D-fructose, L-malic acid, and citric acid were executed using enzymatic UV test kits (R-Biopharm, Darmstadt, Germany). Total titratable acidity (TA) was determined by titration to pH 8.1 with aqueous sodium hydroxide solution (0.25 M) using a 716 DMS Titrino (Metrohm Schweiz, Zofingen, Switzerland) and expressed as citric acid equivalents g/100 g (fruits) or g/100 mL (juices).

Moisture contents of maqui fruit and juice samples were measured by infrared drying at 105 °C (Infrared Moisture Analyzer, Sartorius, Göttingen, Germany). All determinations described above were performed in duplicate, except for mineral analyses, which were conducted in triplicate.

3. Results and discussion

3.1. Identification of anthocyanins

In this study, eight individual anthocyanins were detected by HPLC-DAD-MS^n in maqui berries and juice (Fig. 1A). Delphinidin and cyanidin 3-glucosides (compounds A5 and A7, respectively) were unambiguously identified using authentic standards. Compounds A1, A2, and A4 showed absorption maxima highly similar to delphinidin 3-glucoside (Table 1). Since MS^2 fragmentation pattern of the corresponding parent ions revealed a strong signal at *m*/*z* 303, these compounds were assigned to delphinidin derivatives. Furthermore, MS^2 experiments of the quasi-molecular ions of compounds A1 and A4 revealed a characteristic loss of 294 Da, indicating a hexose-pentose moiety. In addition, compound A1 exhibited an additional consecutive loss of 162 Da corresponding to a hexose residue. These findings are in good agreement with the reports of Escribano-Bailón et al. (2006), Gironés-Vilaplana et al. (2012), Ruiz et al. (2010) and Schreckinger et al. (2010), who characterized these pigments as delphinidin

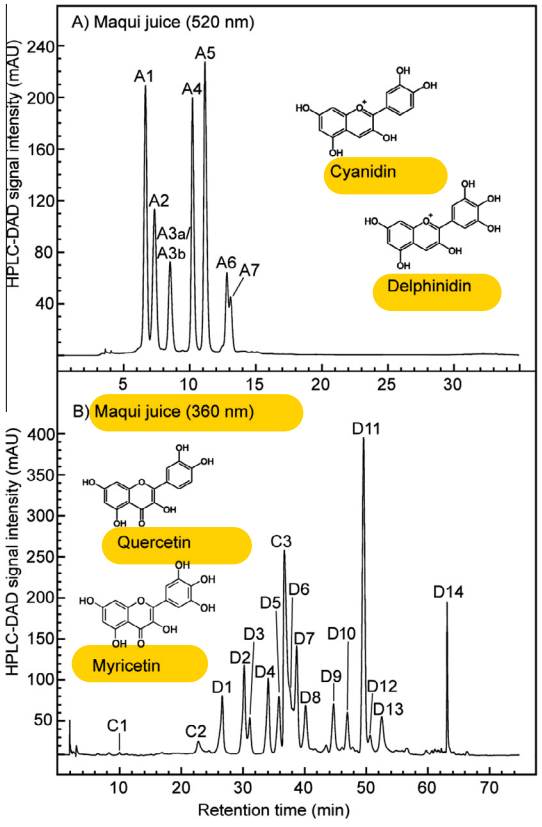

Fig. 1. HPLC separation of anthocyanins and non-anthocyanin phenolic compounds in juice of maqui monitored at 520 (A) and 360 nm (B), respectively. For peak assignment, see Table 1.

Table 1
HPLC retention times, UV/Vis absorption and mass spectral data of phenolic compounds detected in maqui samples.[a]

Peak	Identity	t_R [min]	HPLC-DAD λ_{max} [nm]	$[M]^+$/ $[M-H]^-$ m/z	HPLC–ESI(±)–MS^2 m/z (% base peak)	HPLC-ESI(±)-MS^3 m/z (% base peak)
Anthocyanins						
A1	del-3-sam-5-glc	6.5	524, 344, 275	759	[759]: 303 (100), 465 (68), 597 (46)	[759 → 303]: 233 (100), 165 (16)
A2	del-diglc	7.2	524, 343, 275	627	[627]: 465 (100), 303 (82)	[627 → 465]: 303 (100)
A3a	cya-3-sam-5-glc	8.3	516, 332, 278	743	[743]: 287 (100), 581 (78), 449 (74)	n.a.
A3b	cya-diglc	8.4	516, 332, 278	611	[611]: 449 (100), 287 (52)	[611 → 449]: 287 (100)
A4	del-3-sam	10.0	527, 348, 277	597	[597]: 303 (100)	[597 → 303]: 257 (100), 581 (83), 213 (42)
A5	del-3-glc	10.9	527, 348, 277	465	[465]: 303 (100)	[465 → 303]: 257 (100), 191 (30), 161 (30)
A6	cya-3-sam	12.5	519, 281	581	[581]: 287 (100)	[581 → 287]: 199 (100), 121 (31)
A7	cya-3-glc	12.8	518, 281	449	[449]: 287 (100)	[449 → 287]: 241 (100), 215 (89), 189 (43)
Non-anthocyanin phenolics						
Ellagic acids						
C1	HHDP-hex	10.1	296	481	[481]: 319 (100)	[481 → 319]: 167 (100), 301 (10)
C2	granatin B	22.9	276	951	[951]: 933 (100)	[951 → 933]: 613 (100), 445 (76), 301 (15)
C3	ellagic acid	36.8	368, 252	301	[301]: 301 (100), 185 (80)	n.a.
Flavonols						
D1	myrc-3-galloyl-glc	26.7	356, 292 (sh), 264	631	[631]: 479 (100), 316 (16), 317 (11)	[631 → 479]: 316 (100), 317 (50)
D2	myrc-3-gal	30.3	356, 298 (sh), 258	479	[479]: 316 (100), 317 (76), 179 (12)	[479 → 316]: 179 (100), 191 (49), 271 (48), 273 (30)
D3	myrc-3-glc	31.2	356, 298 (sh), 260	479	[479]: 317 (100), 316 (99), 271 (9)	[479 → 317]: 179 (100), 151 (84), 271 (80)
D4	querc-galloyl-hex	34.2	354, 262	615	[615]: 463 (100), 301 (17)	[615 → 463]: 301 (100), 300 (37), 151 (5)
D5	querc-galloyl-hex	35.9	358, 254	615	[615]: 463 (100), 301 (12)	[615 → 463]: 301 (100), 300 (78), 271 (5)
D6	querc-3-rut	38.2	354, 256	609	[609]: 301 (100), 300 (36), 271 (9)	[609 → 301]: 151 (100), 271 (42), 181 (16), 179 (14)
D7	querc-3-gal	38.8	352, 256	463	[463]: 301 (100)	[463 → 301]: 271 (100), 151 (73), 256 (41), 179 (18)
D8	querc-3-glc	40.3	352, 256	463	[463]: 301 (100), 179 (16)	[463 → 301]: 179 (100), 151 (83), 301 (49), 273 (48)
D9	querc-3-xyl	44.8	354, 256	433	[433]: 301 (100)	[433 → 301]: 255 (100), 271 (66), 179 (29), 151 (9)
D10	querc-3-ara	47.0	354, 254	433	[433]: 301 (100)	[433 → 301]: 179 (100), 255 (59), 273 (43), 151 (27)
D11	dimethoxy-querc	49.7	346, 252	659	[659]: 329 (100), 314 (18), 271 (17)	[659 → 329]: 314 (100), 315 (19), 271 (8) [659 → 314]: 271 (100), 299 (40), 287 (34)
D12	kaemp hex	50.7	334, 270	447	[447]: 285 (100)	[447 → 285]: 241 (100), 199 (50), 285 (18)
D13	myrc	52.6	372, 254	317	[317]: 179 (100), 151 (37)	[317 → 179]: 151 (100)
D14	querc	63.2	370, 256	301	[301]: 151 (100), 179 (56), 273 (45)	n.a.

[a] Abbreviations: ara, arabinoside; cya, cyanidin; del, delphinidin; gal, galactoside; glc, glucoside; hex, hexoside; HHDP, hexahydroxydiphenoyl; kaemp, kaempferol; myrc, myricetin; n.a., not available; querc, quercetin; rut, rutinoside; sam, sambubioside; xyl, xyloside. sh, shoulder; t_R, retention time; λ_{max}, wavelength of UV/Vis absorption maxima.

3-sambubioside-5-glucoside (compound A1) and delphinidin 3-sambubioside (compound A4). Anthocyanin derivatives of the sambubioside type were previously described in diverse berries such as elderberry (*Sambucus nigra* L.), red currant (*Ribes rubrum* L.), and bilberry (*Vaccinium myrtillus* L.) (Du, Jerz, & Winterhalter, 2004; Wu et al., 2004). The delphinidin derivative A2 showed two sequential losses of 162 Da, suggesting the elimination of two hexose moieties. Previously, Escribano-Bailón et al. (2006), Gironés-Vilaplana et al. (2012), Ruiz et al. (2010) and Schreckinger et al. (2010) identified this pigment to be delphinidin 3,5-diglucoside. Recently, Ruiz et al. (2014) identified a rather unusually substituted delphinidin 3,7-diglucoside in calafate (*Berberis microphylla* G. Forst) berries by NMR spectroscopy. Due to the lack of NMR spectra in the present study, the identification of compound A2 and A3b was limited to delphinidin and cyanidin diglucosides, respectively. By analogy to the above-described identification of delphinidin derivatives, several homologous cyanidin derivatives were identified (compounds A3a, A3b, A6, and A7).

Interestingly, anthocyanins in maqui samples mainly consisted of delphinidin and cyanidin derivatives with one or two glycosyl moieties. In nature, anthocyanin glycosides are most frequently occurring, since their stability is superior to that of the respective aglycone. Furthermore, additional acylation of the anthocyanin sugar residues, as for example in black carrot (*Daucus carota* ssp. *sativus* var. *atrorubens* Alef.), has been referred to be responsible for an additionally enhanced pigment stability by sterically protecting the anthocyanin aglycone from hydrolytic degradation (Sadilova et al., 2006). Therefore, compared to black carrot, maqui products are expected to require adequate additional technological measures for ensuring sufficient color retention during food processing and storage.

3.2. Anthocyanin content

The anthocyanin content in maqui determined by HPLC and the pH-differential method are presented in Table 2. As expected, dried maqui berries exhibited the highest total anthocyanin content (TAC) of 36.9 ± 3.2 g/kg of dried berries (39.1 g/kg dry weight (DW)), comprising high proportions of delphinidin-glycosides (78%), as compared to cyanidin-glycosides (22%). The TAC in fresh maqui berries amounted to 26.1 g/kg fresh weight (FW), although their TAC on dry weight basis (68.3 g/kg DW) was about two times higher than in the dried berries. The presented results suggest a substantial degradation of anthocyanins during microwave-assisted vacuum drying at temperatures up to 80 °C (pop dry® process). The particular sensitivity of maqui anthocyanins was also demonstrated by a considerable loss during processing of the fresh berries (26.1 ± 1.1 g/kg FW) to juice (11.6 ± 0.1 g/L FW).

Most interestingly, in fresh maqui fruits, higher proportions of glycosylated cyanidins (52%) were determined, whereas delphinidin derivatives were less abundant (48%). After juice processing, the proportion of delphinidin-glycosides increased to 83% (Table 2). While the absolute concentrations of delphinidin derivatives were only slightly diminished, a substantial loss of cyanidin derivatives was responsible for the losses observed during juice production in maqui (86% total cyanidin reduction). Although a substantial amount of anthocyanins might have been retained in the pomace, these results indicate the particular sensitivity of the present cyanidin derivatives towards thermal degradation. In particular, since the proportion of delphinidin derivatives was similarly high in dried fruits (78% of total anthocyanins), further evidence for the preferred thermal cyanidin degradation during

Table 2
Total anthocyanin contents (TAC), total monomeric anthocyanins (TMAC), polymeric color [%], total phenolics (Folin) and antioxidant capacity (FRAP, TEAC) in maqui samples.[a,b,c]

Peak	Compound	Fresh maqui fruits	Maqui juice	Dried maqui fruits
Anthocyanin contents by HPLC-DAD analyses [g/kg FW; g/L juice]				
A1	del-3-sam-5-glc	4.3 ± 0.1	3.2 ± 0.0	8.1 ± 0.9
A2	del-diglc	2.5 ± 0.0	2.0 ± 0.0	15.9 ± 1.4
A3	cya-3-sam-5-glc (A3a) + cya-diglc (A3b)	7.8 ± 0.6[d]	1.1 ± 0.0[d]	6.0 ± 0.5[d]
A4	del-3-sam	3.1 ± 0.0	2.2 ± 0.0	1.2 ± 0.1
A5	del-3-glc	2.6 ± 0.0	2.2 ± 0.0	3.8 ± 0.3
A6	cya-3-sam	5.9 ± 0.5[e]	0.9 ± 0.0[e]	1.9 ± 0.1[e]
A7	cya-3-glc			
Total anthocyanins		26.1 ± 1.1	11.6 ± 0.1	36.9 ± 3.2
Anthocyanin contents by pH-differential method [g/kg; g/L] and polymeric color [%]				
Total monomeric anthocyanins		12.6 ± 1.5	7.4 ± 0.9	21.1 ± 2.1
Polymeric color		9 ± 0%	35 ± 1%	22 ± 2%
Total phenolics [g/kg FW; g/L juice] and antioxidant capacity [mmol/kg FW; mmol/L juice]				
Folin–Ciocalteu		19.7 ± 0.9	7.3 ± 0.2	32.0 ± 2.1
FRAP		66.7 ± 3.8	45.8 ± 0.0	116.0 ± 0.5
TEAC		73.6 ± 2.1	63.7 ± 1.6	154.6 ± 8.8

[a] Abbreviations: cya, cyanidin; del, delphinidin; FW, fresh weight; gal, galactoside; glc, glucoside; rut, rutinoside; sam, sambubioside; n.d., not detected.
[b] Moisture content for calculation of concentrations per kg dry matter (DM) were as follows: dried maqui fruits 5.5 ± 1.9%; fresh maqui fruits 61.8 ± 0.6; maqui juice 81.7 ± 0.0.
[c] Values expressed as means of triplicate determinations ± standard deviation.
[d] Calculated as sum of cya-3-sam-5-glc (A3a) and cya-diglc (A3b).
[e] Calculated as sum of cya-3-sam (A6) and cya-3-glc (A7).

the drying process applied is provided. Further study is required to elucidate whether enzymatic or thermal degradation or combinations of the two play a decisive role in degrading maqui anthocyanins. Generally, high temperatures and enhanced oxidation reactions during thermal processing are responsible for anthocyanin losses. In addition, the presence of oxygen has been shown to accelerate degradation by a direct oxidative mechanism as well as by representing a co-substrate for oxidizing enzymes. For instance, polyphenoloxidase catalyzes the oxygen-dependent oxidation of non-anthocyanin phenolics to corresponding highly reactive *o*-quinones, which then interact with anthocyanins to form brown condensation products (Jackman, Yada, & Tung, 1987). Nevertheless, anthocyanin degradation might be prevented by microencapsulation of anthocyanin extracts. For instance, stabilization of anthocyanins and non-anthocyanin phenolics applying microencapsulation was reported recently (Vidal J. et al., 2013).

For further characterization of anthocyanin degradation, the polymeric color content (browning index, BI) was studied, representing an index of anthocyanin degradation as a result of polymerized brown colored anthocyanin-tannin complexes (Giusti & Wrolstad, 2005). The BI of fresh maqui fruits (BI = 9%) significantly increased due to juice processing, yielding a BI of 35% in the corresponding juice. Likewise, the drying process (pop dry® process) led to a BI of 22% in dried maqui berries, analogously indicating the anthocyanin degradation.

To support the HPLC data (Table 2), in addition to TAC, the monomeric anthocyanin content (TMAC) was spectrophotometrically determined. Although differences between HPLC and spectrophotometric values have been frequently reported (Lee, Rennaker, & Wrolstad, 2008), the exceptionally high anthocyanin content of maqui and derived products was confirmed by these means. For instance, fresh maqui berries (TMAC = 12.6 ± 1.5 g/kg FW; TAC = 32.1 ± 1.7 g/kg FW) contained substantially higher levels than other anthocyanin-rich fruits and vegetables such as black currant (TMAC = 2.9 g/kg FW; TAC = 4.8 g/kg FW) and elderberry (TAC = 13.8 g/kg FW) as well as red cabbage and red radish (TAC = 3.2 and 1.0 g/kg FW, respectively) (Nour, Trandafir, & Ionica, 2011; Wu et al., 2006). Previous studies on maqui fruits reported similarly high anthocyanin concentrations, although a certain variation due to the natural inhomogeneity of the plant materials as well as differing analytical methodologies is to be considered. Thus, significant lower TACs from 1.4 to 8.3 g/kg of fresh maqui berries were reported after methanolic extraction and quantitation by HPLC (Escribano-Bailón et al., 2006; Ruiz et al., 2010). In contrast, Fredes, Montenegro, Zoffoli, Gómez, and Robert (2012) investigated the TMAC of two wild populations of maqui fruits harvested at different maturity stages in central Chile. The late maturity stage resulted in the highest anthocyanin contents ranging from 7.9 to 8.8 g/kg FW. Additionally, Fredes et al. (2014) reported significantly different TACs (7.6 to 19.7 g/kg FW) in wild maqui berries depending on their geographical origins in Chile.

3.3. Identification of non-anthocyanin phenolics

Besides anthocyanins, 17 non-anthocyanin phenolics were detected in maqui berries and juice obtained therefrom, among them three ellagic acids (compounds C1–C3) and 14 flavonols (compounds D1–D14) as depicted in Fig. 1B and Table 1. Compound C1 revealed a quasi-molecular ion $[M-H]^-$ at *m*/*z* 481 producing a fragment at *m*/*z* 319 in the MS^2 experiment, thus indicating the release of a hexose (162 Da). The subsequent loss of water produced a further daughter ion at *m*/*z* 301, being typical of ellagic acids. Moreover, the daughter ion at *m*/*z* 319 showed a characteristic loss of 152 Da in the MS^3 experiment, possibly representing the loss of a gallic acid moiety. Since Fischer et al. (2011) described an $[M-H]^-$ ion at *m*/*z* 481 as a hexahydroxydiphenoyl-hexoside (HHDP-hexoside) exhibiting a similar fragmentation pattern, compound C1 was tentatively assigned as HHDP-hexoside. A pseudo-molecular ion $[M-H]^-$ at *m*/*z* 301 was also observed for compound C3, which then was identified as ellagic acid by comparison of its retention time, UV/Vis absorption and mass spectra to those of an authentic standard. As previously reported for maqui by Gironés-Vilaplana et al. (2012), compound C2 was tentatively characterized as the ellagitannin granatin B. This compound produced a parent ion at *m*/*z* 951 with characteristic MS^2 and MS^3 fragmentation patterns as described for granatin B in pomegranate (*Punica granatum* L.) by Fischer et al. (2011). To the best of our knowledge, the putative HHDP-hexoside (C1) and ellagic acid (C3) have so far not been detected in maqui berries. In contrast, ellagic acid hexoside (*m*/*z* 463) and ellagic acid rhamnoside (*m*/*z* 447) were not detected,

although being reported previously (Gironés-Vilaplana et al., 2012).

In agreement with Gironés-Vilaplana et al. (2012), several acylated and glycosylated flavonols were found in maqui. Mainly myricetin and quercetin derivatives were detected, producing characteristic daughter ions at *m/z* 317 and 301 in the MS^2 experiment, respectively. Noteworthy, quercetin showed the same quasi-molecular ion $[M-H]^-$ at *m/z* 301 like ellagic acid. Matching with commercial standards, however, quercetin ions generated typical daughter ions at *m/z* 271, 179 and 151 in the MS^2 and MS^3 experiments, whereas ellagic acid fragmentation yielded a predominant daughter ion at *m/z* 185 as well as a much higher proportion of non-fragmented ions at *m/z* 301 with the same fragmentation settings. The flavonols eluting in the range of 26.7–47.0 min were mono-substituted with different sugar residues, as shown by the loss of 308 Da for rutinoside as well as 162 Da for galactoside and glucoside, and 132 Da for xyloside and arabinoside residues, respectively. The respective glycosyl moieties were identified by comparison of their elution behavior with data published by Gironés-Vilaplana et al. (2012). According to their polarity, the compounds eluted in the following order: myricetin 3-galloyl-glucoside (D1), myricetin 3-galactoside (D2), myricetin 3-glucoside (D3), and quercetin 3-rutinoside (D6), quercetin 3-galactoside (D7), quercetin 3-glucoside (D8), quercetin 3-xyloside (D9), and quercetin 3-arabinoside (D10).

Furthermore, two yet unknown quercetin derivatives (D4 and D5) were detected. Both compounds revealed an $[M-H]^-$ ion at *m/z* 615 producing a typical quercetin-hexoside daughter ion at *m/z* 463 in the MS^2 experiments, probably indicating the loss of a gallic acid moiety (152 Da). Hence, the quercetin derivatives were tentatively identified as quercetin galloyl-hexosides. In addition to these findings, compound D12 showed a quasi-molecular ion $[M-H]^-$ at *m/z* 447 with derived fragments at *m/z* 285 in the MS^2 and MS^3 experiments, most likely representing a kaempferol hexoside due to identical mass spectral pattern as compared to an authentic kaempferol 3-glucoside standard.

The major peak (D11) showed a molecular ion $[M-H]^-$ at *m/z* 659 revealing an abundant daughter ion at *m/z* 329, potentially representing a di-methoxylated quercetin ion $[M-330-H]^-$. The loss of 330 Da could not be assigned to any particular acyl or glycosyl moiety and, according to its late elution (t_R = 49.7 min), the compound is unlikely to be highly glycosylated or acylated. Therefore, the observed ion at *m/z* 659 might represent an intermolecular cluster of the form $[2M-H]^-$, which was formed *in-source* due to its high concentration. The daughter ion at *m/z* 329 exhibited further MS^3 daughter ions at *m/z* 314 and 299, possibly resulting from the consecutive loss of two methyl groups (15 Da). The UV/Vis absorption maxima of the parent compound (346 and 252 nm) showed a hypsochromic shift compared to the non-methoxylated quercetin species and, thus, supported the hypothesized tentative structure of a di-methoxylated quercetin species. Nevertheless, further study will be required to unequivocally identify compound D11.

Moreover, myricetin (D13) and quercetin (D14) were detected by comparison of their retention times, UV/Vis and mass spectral data with those of commercial standards and previously published data, respectively (Regos et al., 2009; Kammerer et al., 2004). Besides these findings, Céspedes et al. (2010) and Schreckinger et al. (2010) reported the presence of several hydroxycinnamic acids and proanthocyanidins in ethanol and fractionated acetone extracts, which could not be found in the present investigation.

3.4. Total phenolics and antioxidant activity

Total phenolic levels derived from the Folin–Ciocalteu test showed a good linear correlation to TACs as deduced by HPLC (R^2 = 0.91, while a lower coefficient of determination was found for FRAP (R^2 = 0.74) and TEAC (R^2 = 0.56) assays. Photometrically determined TMACs exhibited higher correlations (R^2 = 0.98, Folin; R^2 = 0.99, FRAP; R^2 = 0.92, TEAC). The three test assays yielded highest values for dried berries of maqui, followed by the fresh fruits and the juice (Table 2). The exceptionally high total phenolic levels and antioxidant activities in maqui samples are most likely due to their outstandingly high anthocyanin contents, since the anthocyanin-rich fraction of maqui berries was reported to contribute the most to their overall antioxidant potential (Miranda-Rottmann et al., 2002).

According to Ruiz et al. (2010), antioxidant activity (TEAC) amounted to 88 mmol trolox equivalents/kg FW in fresh maqui fruits, thus being in the similar range as in our study (74 ± 2 mmol trolox equivalents/kg FW). For comparison, juices of popular "superfruits" such as pomegranate (42 mmol trolox equivalents/L), açai (13 mmol trolox equivalents/L) and cranberry (10 mmol trolox equivalents/L) were previously reported (Seeram et al., 2008) to exhibit drastically lower antioxidant capacities compared to the maqui juice sample (64 ± 2 mmol trolox equivalents/kg FW). As a consequence, the consumption of maqui has been associated with remarkable health benefits (Miranda-Rottmann et al., 2002; Céspedes et al., 2008). Several *in vitro* studies demonstrated the inhibition of adipogenesis and inflammation by maqui anthocyanins and the prevention of LDL oxidation (Schreckinger, et al., 2010; Miranda-Rottmann et al., 2002). To date, *in vivo* health effects of maqui consumption have been scarcely investigated, and *in vivo* bioavailability and metabolism studies of its constituents are lacking.

3.5. Total lipids and fatty acid composition

Table 3 provides an overview of the total lipid contents, individual fatty acid contents (FA, determined as methyl esters) and their relative contribution to the total lipids of the entire fruits, i.e. the seeds were not separated prior to analyses. In addition to the above-described fruit and juice samples, the pomace of the maqui juice production was examined as they could represent a low-cost substrate for fruit oil production. The total lipid contents of fresh maqui berries (2.9 g/100 g of FW) markedly exceeded those usually observed in other integral berries (<1 g/100 g of FW, including seeds), except for those of sea buckthorn (3.5 g/100 g of FW; *Hippophae* sp., Souci, Fachmann, & Kraut, 1989/90).

The high lipid content of the fresh berries might be due to their low fruit pulp:seed ratio of ~1:1 (w/w). When the seeds were separated during juice production, total lipid contents as well as the proportions of total fatty acids in the total lipids were drastically reduced (Table 3). Thus, total lipids in the obtained juice of fresh maqui fruits (0.3 g/100 g of FW) consisted of lipids other than fatty acid-rich compounds such as triacylglycerides. Maqui lipids only contained <15% of saturated fatty acids (SFA), mostly myristic, palmitic and stearic acid (Fig. 2.). Major monounsaturated fatty acids (MUFA) were oleic (C18:1*n*−9) and vaccenic acid (C18:1*n*−7), while linoleic (C18:2*n*−6c) and α-linolenic acid (C18:3*n*−3) represented the predominant polyunsaturated fatty acids (PUFA).

For comparison, other berries rich in anthocyanins as well as MUFAs and PUFAs in the seed oils such as black currant (*Ribes nigrum* L.) could be clearly differentiated from maqui oils by the presence of γ-linolenic acid (C18:3*n*−6, 12.6%). Moreover, black currant lipids were also found to be rich in linoleic acid (47.5%), α-linolenic (14.5%), and stearidonic (18:4*n*3, 2.7%) acid (Tahvonen, Schwab, Linderborg, Mykkänen, & Kallio, 2005).

In summary, the lipid fraction from maqui was found to be highly unsaturated (up to 86%) and high ratios of PUFA/SFA, ranging from 3.2 to 3.5, were determined. Diets rich in PUFA have been related to an increased ratio of HDL to LDL cholesterol, being

Table 3
Total lipid contents [g/100 g FW], total FAs content [g/100 g FW] and FAs contribution to total FAs content [% (w/w)] in maqui samples.[a,b,c]

	Fresh maqui fruits	Maqui juice	Maqui pomace	Dried maqui fruits
Total lipid content[c]	2.87 ± 0.19	0.29 ± 0.03	3.78 ± 0.01	8.13 ± 0.33
Total FAs[c]	2.35 ± 0.32	0.002 ± 0.001	3.77 ± 0.03	7.13 ± 0.49
Contribution of FA to total FAs [%]				
C12:0	0.51 ± 0.02	10.81 ± 0.42	0.48 ± 0.01	0.49 ± 0.01
C14:0	1.07 ± 0.04	14.79 ± 0.44	1.04 ± 0.00	1.05 ± 0.02
C15:0	0.02 ± 0.00	n.d.	0.03 ± 0.01	0.02 ± 0.00
C16:0	8.63 ± 0.11	44.90 ± 0.30	9.68 ± 0.02	8.70 ± 0.04
C18:0	3.47 ± 0.09	14.79 ± 1.0	3.46 ± 0.04	3.29 ± 0.05
C20:0	0.13 ± 0.01	n.d.	0.15 ± 0.01	0.13 ± 0.00
C22:0	0.18 ± 0.01	n.d.	0.27 ± 0.02	0.19 ± 0.00
C24:0	0.13 ± 0.01	n.d.	0.11 ± 0.13	0.14 ± 0.00
C16:1*n*−7	0.35 ± 0.01	n.d.	0.50 ± 0.01	0.37 ± 0.02
C18:1*n*−9	33.49 ± 0.11	14.71 ± 1.29	32.26 ± 0.09	33.28 ± 0.24
C18:1*n*−7	3.81 ± 0.01	n.d.	3.50 ± 0.05	3.72 ± 0.01
C20:1*n*−9	0.24 ± 0.01	n.d.	0.22 ± 0.00	0.22 ± 0.00
C18:2*n*−6	46.00 ± 0.35	n.d.	44.89 ± 0.33	46.31 ± 0.09
C18:3*n*−3	1.96 ± 0.04	n.d.	3.39 ± 0.21	2.09 ± 0.03

[a] Abbreviations: FA, fatty acid, determined as methyl esters; FW, fresh weight; n.d., not detected.
[b] Values expressed as means of duplicate determinations ± standard deviation.
[c] Moisture contents were as follows: dried maqui fruits 5.5 ± 1.9%; fresh maqui fruits 61.8 ± 0.6; maqui juice 81.7 ± 0.0; maqui pomace 37,6 ± 0.4.

potentially helpful for preventing cardiovascular diseases (Mensink, Zock, Kester, & Katan, 2003).

3.6. Mineral and trace element content

The mineral and trace element compositions of maqui are shown in Table 4. Fresh maqui fruits were characterized by their high content of K (3683 ± 111 mg/kg), being always abundant in plants. Maqui reached similar K contents as described for K-rich bananas (3930 mg/kg, *Musa paradisiaca* L., Souci et al., 1989/90). Ca content of maqui berries (1558 ± 33 mg/kg) was more than threefold higher than that in the commonly Ca-rich black currant (460 mg/kg, *Ribes nigrum* L., Souci et al., 1989/90). The Mg content in fresh maqui fruits (309 ± 10 mg/kg) was similar to those of Mg-rich raspberries (300 mg/kg, *Rubus idaeus* L., Souci et al., 1989/90).

The trace elements exhibited highest concentrations in dried maqui berries, followed by the fresh fruits and the derived juice (Si > Fe > Ba > Mn > Zn > Cu > Mo > Cr) and concentrations ranged from 0.040 ± 0.002 (Cr) to 23 ± 1 mg/kg (Si), i.e. in fresh maqui fruits (Table 4). In comparison, concentrations of further trace elements were found to be very low (V and Co) or below/scarcely below the detection limit (Sn, As, Sb, Zr, Cd and Hg) in all samples.

The essential elements Si, Mo, Fe, Cu, Cr and Mn in maqui samples exhibited contents similar to other anthocyanin-rich berries. For instance, Cu, Fe, Zn and Mn contents were similar in fresh maqui fruits as compared to those in black currant (Cu = 1.9 mg/kg), red currant (Fe = 9.7 mg/kg), raspberry (Zn = 2.9 mg/kg) and strawberry (Mn = 3.2 mg/kg) (Skesters et al., 2014). Nevertheless, the Mo concentration in 100 g fresh maqui fruits (0.03 mg/100 g) represented about 66% of the required intake (Recommended Dietary Allowances, RDA) per day per adult person (male or female > 19 years) according to the guidelines of the USDA National Agricultural Library. Additionally, Fe (17.2% of the RDA, male > 19 years) and Cu (17.5% of the RDA, male or female > 19 years) were determined in high quantities, i.e. in 100 g fresh maqui fruits. Only Adequate Intakes (AI) per day (adult person >19 years) are listed regarding the essential elements Cr and Mn. According to the AI parameter, consumption of 100 g fresh fruits would cover 11.5% (male)/16.1% (female) and 17.2% (male)/21.8% (female) of the AIs of Mn and Cr, respectively.

One pollutant being toxic for human health even in microgram quantities was Ni (0.103–0.315 mg/kg). However, according to the guideline stipulating threshold values for toxicologically relevant

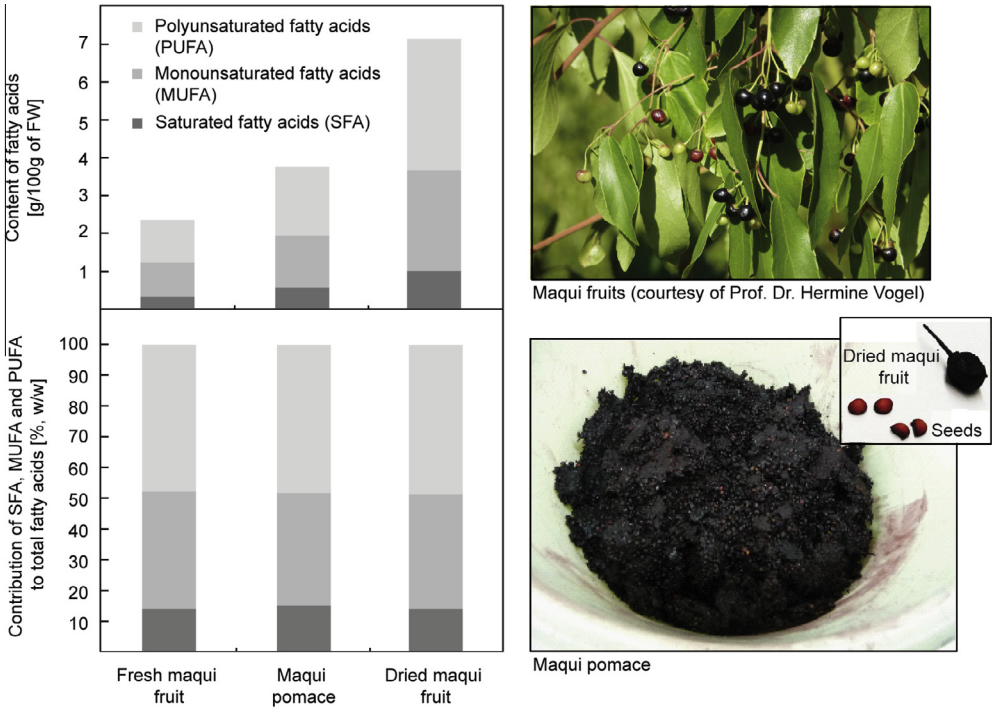

Fig. 2. Total fatty acid (determined as methyl esters, FAs) contents and the relative contribution of saturated (SFA), mono (MUFA) – and polyunsaturated (PUFA) fatty acids to total FAs [% (w/w) of FAs contents] in oils of maqui products and by-products thereof (left). Photographs of maqui berries, seeds, and pomace (right).

Table 4
Minerals, trace elements, sugars, edible acids and titratable acidity of maqui samples.[a]

Elements[b]	Fresh maqui fruit [mg/kg FW]	Maqui juice [mg/kg FW]	Dried maqui fruit [mg/kg]
Na	4.8 ± 0.1	12.1 ± 0.4	78.5 ± 4,7
K	3683 ± 111	3380 ± 17	7369 ± 162
Mg	309 ± 10	163 ± 3	769 ± 11
Ca	1558 ± 33	481 ± 12	3087 ± 12
P	576 ± 25	161 ± 2	1263 ± 12
S	206 ± 10	40 ± 1	688 ± 12
Cl^-	159 ± 10	220 ± 1	878 ± 7
V	0.014 ± 0.003	0.003 ± 0.001	0.115 ± 0.006
Cr	0.040 ± 0.002	0.078 ± 0.005	0.167 ± 0.026
Mo	0.297 ± 0.008	0.105 ± 0.001	0.040 ± 0.009
Mn	3.9 ± 0.2	1.4 ± 0.1	11.1 ± 0.4
Fe	13.7 ± 10.7	3.8 ± 0.1	50.9 ± 1.0
Co	0.008 ± 0.001	0.005 ± 0.000	0.026 ± 0.001
Cu	1.58 ± 0.06	1.06 ± 0.1	3.82 ± 0.01
Zn	3.26 ± 0.07	3.28 ± 0.03	8.19 ± 0.19
Si	23 ± 1	11 ± 0	117 ± 15
Ba	4.71 ± 0.20	2.13 ± 0.02	8.71 ± 1.10
Sn	nq	nq	nq
As	nq	nq	nq
Sb	nq	nq	nq
Zr	nq	nq	nq
Cd	nq	nq	nq
Hg	nq	nq	nq
Ni	0.149 ± 0.011	0.103 ± 0.002	0.315 ± 0.021
Al	2.9 ± 0.2	1.3 ± 0.0	54.4 ± 1.7
Sugars and acids[c]	[g/100 g FW]	[g/100 mL]	[g/100 g]
Sucrose	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
D-Glucose	4.6 ± 0.0	5.5 ± 0.0	14.3 ± 0.1
D-Fructose	4.3 ± 0.0	5.1 ± 0.0	13.9 ± 0.0
Citric acid	1.7 ± 0.0	2.1 ± 0.0	2.5 ± 0.0
Malic acid	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0
Titratable acidity	2.0 ± 0.0	1.9 ± 0.0	2.8 ± 0.0

nq: not quantifiable.
[a] Moisture contents were as follows: dried maqui fruits 5.5 ± 1.9%; fresh maqui fruits 61.8 ± 0.6%; maqui juice 81.7 ± 0.0%.
[b,c] Values expressed as means of triplicate[b]/duplicate[c] determinations ± standard deviation.

substances in food being listed by the European Food Safety Authority (EFSA) and the Food and Drug Administration (FDA), the critical levels were not exceeded. In addition to Ni, renal function and hypertension was reported to be affected by the exposure to Ba and Ba compounds. However, the Ba concentrations in 100 g maqui fruits (fresh and dried) and the juice (2.13–8.71 mg/kg) were below the no-observed-adverse-effect level (NOAEL, 0.21 mg barium/kg body weight per day) being critical in humans for toxicity.

Previous studies have indicated that the ingestion of Al may be involved in the progression of Alzheimer's disease (Walton, 2013). On 22 May 2008 the EFSA Panel on Food Additives, Flavorings, Processing Aids and Food Contact Materials established a tolerable weekly intake (TWI) of 1 mg of Al per kilogram of body weight. Al concentration in the analyzed fruit samples ranged from 1.3 to 2.9 mg/kg of FW and 54.4 mg/kg of DM in dried maqui berries and therefore, seemingly being irrelevant.

In conclusion, the investigated maqui fruit samples were shown to be a potentially interesting dietary source for K, Ca and Mg revealing high levels of respective minerals as compared to other fruits. The high amount of Mo in the examined maqui berries, which might enhance their potential as healthy coloring food pigments, merits further investigation based on a larger sample set.

3.7. Sugars and edible acids

Besides traces of sucrose (<0.05 g/100 g FW), fresh maqui fruits contained equal amounts of D-glucose (4.6 g/100 g FW) and D-fructose (4.3 g/100 g FW), suggesting strong invertase activity (Table 4). By analogy, higher concentrations of D-glucose (2.8 g/100 g FW) and D-fructose (3.7 g/100 g FW) along with a low sucrose concentration (0.2 g/100 g FW) were found in other anthocyanin-rich berries such as black currant (Souci et al., 1989/90). Citric acid was determined to be the major acid in all samples, while malic acid contents were negligible (Table 4). Titratable acidity levels were comparable to those of citric acid quantities. For comparison, citric acid was shown to be the major acid (2.9 g/100 g FW) in black currant, whereas its titratable acidity level was slightly higher (Souci et al., 1989/90). Concerning the juice and dried fruits of maqui samples, higher contents of sugars and edible acids were observed as compared to the fresh fruit sample.

4. Conclusion

This study clearly highlights the enormous potential of maqui as a pigment- and antioxidant-rich "superfruit". It is therefore suitable as a healthy coloring foodstuff or additive in acidic food products due to its outstandingly high concentration of anthocyanins. For instance, fresh maqui berries exhibited twice (elderberry) and up to 26 times (red radish) higher total anthocyanin contents compared to other anthocyanin-rich fruits and vegetables. At the same time, the antioxidant capacity was similarly high in maqui fruits and the derived juice. During juice production, an oil-rich pomace was obtained which might be exploited for seed oil production. Maqui fruits and, in particular, the pomace obtained after de-juicing was shown to be rich in health-promoting polyunsaturated fatty acids. Thus, the pomace might be a low-cost source for maqui fruit oil production. In addition, maqui berries appear to be a good source of K, Ca, Mg and Mo, exhibiting similarly high contents than other anthocyanin-rich berries. The moderate sugar content of maqui fruits may support their excellent suitability as low-calorie foodstuff. Thus, maqui represents a high-potential but still under-utilized "superfruit".

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