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Original Research Article

Determination by HPLC-DAD-ESI/MS^n of phenolic compounds in Andean tubers grown in Ecuador

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ABSTRACT

In this work, the phenolic compounds of four Andean tubers grown in Ecuador, such as yacon (*Smallantus sonchifolius*), mashua (*Tropaeolum tuberosum*), melloco (*Ullucus tuberosus*) and purple-sweet potato (*Ipomea batatas*) were analyzed by HPLC–DAD–ESI/MS^n. Non-flavonoid compounds, such as hydroxycinnamic derivatives were identified in yacon, purple sweet potato and melloco samples, accounting for 100, 26 and 15% of the total of phenolic compounds, respectively. Mashua sample revealed the presence of flavan-3-ol monomers that were not found in the other samples, being (-)-epicatechin the most abundant (9.22 μg/g DM). Quercetin-3-*O*-rutinoside (40.6 μg/g DM), kaempferol-*O*-dirhamnosil-hexoside (29.5 μg/g DM) and kaempferol-*O*-dihexoside (46.22 μg/g DM) were the main flavonols present in mashua, melloco and purple sweet potato, respectively, being this last specie which presented the highest concentration in flavonols (89.32 μg/g DM). Purple sweet potato also had anthocyanins (157.16 μg/g DM), not detected in the other samples. The presence of these compounds and the consideration of the total phenolic content suggest the use of these Andean tubers as promising sources of natural antioxidants of wide use in the food industry. Therefore, these tubers could be considered as novel and inexpensive sources of bioactive compounds for their potential use in functional foods and nutraceuticals.

1. Introduction

The chemical properties and simplicity of use of antioxidants have made them a part of many foodstuffs and pharmacological products. The traditional application of antioxidants is their use as additives to confer taste, colour, or to preserve food for the longest possible time. In addition, it is well known the interest in antioxidants attributed to the extensive evidence on the decrease of health disorders under their consumption. Moreover, in recent years more attention is being paid to the study of natural antioxidants present in unexplored or underutilized plant sources due to the safety concerns and limitations on the use of synthetic antioxidants (Shahidi and Ambigaipalan, 2015; Carocho et al., 2018).

Phenolic compounds are natural antioxidants present in the vacuoles of vegetables tissues that generally are involved in plants defence against ultraviolet radiation or pathogenic aggression (Manach et al., 2004). In addition, phenolic compounds may possess anti-inflammatory, anti-cancer, anti-proliferative, anti-viral activities, and exert an effect on capillary fragility and against human platelet aggregation (Del Rio et al., 2013). Among underutilized plant sources, Andean tubers are crops that grow at high-elevation and whose chemical composition and biological potential remain largely unexplored (Carrillo-Hormaza et al., 2015).

Particularly in the Central Andes (Ecuador to Bolivia) (1500 to 4000 m.s.), the highest variability of Andean species has been observed (Tapia et al., 2007); and, in Ecuador, there are unexplored Andean tubers that are produced by small farmers only as subsistence crops, due to the lack of knowledge on their physicochemical properties and potential for industrial application.

For this reason, yacon, mashua, melloco, purple sweet potato and white carrot varieties from Ecuador were analysed in a previous study, observing that they have the same or greater amount of antioxidant

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compounds as compared to species of similar varieties grown in other countries or regions, being important to identify and quantify their individual phenolic compounds (Pacheco et al., 2019).

In addition, some of these phenolic compounds have been identified in Andean tubers cultivated mainly in Peru, Czech Republic and China (Shahidi and Ambigaipalan, 2015; Campos et al., 2018). Gomes da Silva et al. (2018) have recently reported the presence of trans-cinnamoylquinic acids derivatives in yacon syrup. In this sense, yacon extracts have been shown to exert photoprotective effect on dermal cells (Duque et al., 2017).

Chirinos et al. (2008b) showed that mashua tubers partially inhibit the hemolysis of erythrocytes, which could be due to their composition in phenolic compounds. These authors described the presence of hydroxycinnamic and hydroxybenzoic acids, as non-flavonoid compounds, and also flavan-3-ols, procyanidins, flavonols and anthocyanins as flavonoid compounds.

In melloco, the presence of betalains and betacyanins has been observed (Campos et al., 2006). Extracts of this tuber have presented collagenase activity, being a promising candidate to help the regeneration of tissue without scars (Heil et al., 2017). Nevertheless, as far as we know, no studies have described the presence of phenolic compounds in this tuber.

Gras et al. (2017) and Wang et al. (2018) have determined the phenolic profile of some varieties of sweet potato by HPLC-ESI-MS. These authors found the presence of hydroxycinnamic derivatives, flavonols, as quercetin glycosides and anthocyanins, indicating that their content depends considerably on the variety.

Thus, the objective of this study was to identify and quantify by HPLC-DAD-ESI/MS^n the main phenolic compounds present in yacon, mashua, melloco, purple sweet potato and white carrot, whose Ecuadorian varieties have not been sufficiently studied to date, in order to elucidate their potential use in the food industry and health care.

2. Material and methods

2.1. Samples

Andean tubers: yacon (*Smallantus sonchifolius*, var. INIAP-ECU-1247), mashua (*Tropaeolum tuberosum*, var. INIAP-ECU-Izaño), melloco (*Ullucus tuberosus*, var. INIAP-ECU-amarillo-rosa), purple sweet potato (*Ipomea batatas*, var. INIAP-ECU-morado) cultivated in Cotopaxi-Ecuador (2800–3600 m.a.s.l.) and harvested in mid-April, were washed, lyophilized, grounded and stored at −20 °C until analysis.

2.2. Chemicals

Phenolic compound standards (≥90% HPLC) were purchased from Sigma-Aldrich (Madrid, Spain) and Extrasynthese (Barcelona, Spain). Acetonitrile, formic acid and ultrapure water were of HPLC grade from Carlo Erba (Rodano, Italy) and Panreac (Barcelona, Spain). All other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) unless otherwise specified.

2.3. Extraction of phenolic compounds

Extraction and analyses of phenolic compounds were performed applying the methods described by Dueñas et al. (2015). Briefly, 2 g of freeze-dried samples were sonicated and macerated in methanol: TFA ($1^0/_{000}$)–water (80:20, v:v) at 4 °C for 24 h. Subsequently, they were centrifuged at 7000 × *g* and 4 °C for 30 min in a super-speed centrifuge (Sorval RC 5B). The extraction process was repeated three times. The extracts were combined and concentrated at 30 °C under vacuum for methanol evaporation.

For phenolic analysis, the dry extracts were dissolved in 20 mL of water. For purification, an aliquot (1 or 2 mL) was passed through a C_{18} Sep-Pak cartridge (Waters, Milford, MA, USA), previously activated with methanol and water. Sugars and polar substances were removed by passing 10 mL of ultrapure water and phenolic compounds were eluted with methanol. Afterwards, extract was concentrated under vacuum in a rotary evaporator (30 °C) and then dissolved in 0.1% TFA: acetonitrile (90:10, v/v) for phenolic compound analysis.

2.4. HPLC–DAD–ESI/MS^n analyses of phenolic compounds

2.4.1. Non-anthocyanin compounds

Samples were analyzed using a Hewlett-Packard 1100MS (Agilent Technologies, Palo Alto, CA) chromatograph equipped with a quaternary pump, diode array detector (DAD) coupled to an HP Chem Station (rev. A.0504) data-processing station. Solvents used were 0.1% formic acid in water (solvent A), and 100% acetonitrile (solvent B). The elution gradient established was 15% B for 5 min, 15–20% B for 5 min, 20–25% B for 10 min, 25–35% B for 10 min, 35–50% B for 10 min, and re-equilibration of the column. The separation of phenolic compounds was performed in a Spherisorb S3 ODS-2 C_8 column (Waters, Millford, USA) (3 µm, 150 mm × 4.6 mm i.d.) operating at 35 °C and a flow rate of 0.5 mL min^{-1}. Double online detection was carried out in the DAD using 280 nm and 370 nm as preferred wavelengths. Mass spectrometer (MS) connected to the HPLC system *via*the DAD cell outlet was used and detection was performed in an API 3200 Qtrap (Applied Biosystems, Darmstadt, Germany) equipped with an ESI source, triple quadrupole ion trap mass analyzer and controlled by the Analyst 5.1 software following the method described by Dueñas et al. (2015). The setting parameters were: zero grade air as the nebulizer gas (30 psi), turbo gas for solvent drying (400 °C, 40 psi), nitrogen served as the curtain (20 psi) and collision gas (medium). The quadrupoles were set at unit resolution. The ion spray voltage was set at −4500 V in the negative mode. The MS detector was programmed to perform a series of two consecutive modes: enhanced MS (EMS) and enhanced product ion (EPI) analysis. EMS was employed to show full scan spectra, to give an overview of all the ions in sample. Settings used were: declustering potential (DP) −45 V, entrance potential (EP) −6 V, collision energy (CE) −10 V.

Spectra were recorded in negative ion mode between *m/z*100 and 1000. EPI mode was further performed with the aim to obtain the fragmentation pattern of the parent ion(s) of the previous experiment using the following parameters: DP: −50 V, EP: −6 V, CE: −25 V, and collision energy spread (CES) 0 V. The non-anthocyanin phenolic compounds were characterized according to their UV and mass spectra and retention times, and comparison with authentic standards when available.

For quantitative analysis, calibration curves were prepared by injection of different standard phenolic compounds in the range of 1–100 µg/mL.

The standards (≥ 90%, HPLC) used in the determination of non-anthocyanin compounds were: caffeic acid (for caffeic acid derivatives; yacon, Table 1); epicatechin, *p*-coumaric acid, isorhamnetin 3-*O*-rutinoside, quercetin 3-*O*-glucoside, quercetin 3-*O*-rutinoside (for catechin and *p*-coumaric derivatives, myricetin and isorhamnetin compounds, and quercetin derivatives; mashua, Table 2); ferulic acid, quercetin 3-*O*-rutinoside, kaempferol 3-*O*-rutinoside, quercetin 3-*O*-glucoside, isorhamnetin 3-*O*-rutinoside (for ferulic compounds, quercetin, kaempferol, quercetin and isorhamnetin derivatives; melloco, Table 3); and, caffeic and ferulic acids, naringenin, *p*-coumaric acid, quercetin 3-*O*-glucoside, kaempferol 3-*O*-glucoside, isorhamnetin 3-*O*-glucoside (for caffeic and ferulic acid derivatives, eriodictyol, *p*-coumaric derivatives; quercetin, kaempferol and isorhamnetin glucosides; purple sweet potato, Table 4).

The concentration of phenolic compounds was calculated; using the respective calibration curve for each peak, obtained by HPLC analysis in the same conditions. Results were expressed as µg/g dry matter (DM).

Table 1
Retention time (Rt), wavelengths of maximum absorption in the visible region (λ_{max}), mass spectral data, tentative identification and quantification (μg/g DM) of non-anthocyanin compounds present in yacon.

Peak	Rt (min)	λ_{max} (nm)	Molecular ion[M-H]$^-$ (m/z)	Main fragments (Da)	Tentative identification	μg/g DM
1	5.1	326	353	191(8), 179(4), 173(3), 161(12), 135(94)	Caffeoylquinic acid	6.66 ± 0.56
2	5.3	324	353	191(100), 179(78), 173(5), 161(8), 135(92)	Caffeoylquinic acid	29.15 ± 3.35
3	5.6	328	371	209(90), 191(100), 179(17), 135(12)	Caffeoylglucaric acid	23.18 ± 3.77
4	5.7	328	397	353(2), 293(16), 235(67), 179(26), 163(6), 161(100), 135(55)	4-*O*-caffeoyl-2,7-anhydro-D-glycero-β-D-galacto-oct-2-ulopyranosonic acid isomer 1	53.03 ± 7.93
5	6.0	328	397	353(3), 293(42), 235(78), 179(25), 163(20), 161(93), 135(19)	4-*O*-caffeoyl-2,7-anhydro-D-glycero-β-D-galacto-oct-2-ulopyranosonic acid isomer 2	42.48 ± 1.91
6	7.7	326	353	191(69), 179(72), 173(92), 161(12), 135(100)	Caffeoylquinic acid	20.17 ± 2.74
7	8.4	326	353	191(100), 179(18), 173(6), 161(21), 135(12)	Caffeoylquinic acid	180.78 ± 21.10
8	11.7	328	353	191(39), 179(9), 173(49), 155(33), 135(38)	Caffeoylquinic acid	47.98 ± 3.02
9	14.1	328	533	371(27), 353(25), 209(92), 191(100), 179(19), 135(32)	Dicaffeoylaltraric acid isomer 1	46.06 ± 2.68
10	14.7	328	533	371(21), 353(19), 209(100), 191(74), 179(10), 135(26)	Dicaffeoylaltraric acid isomer 2	6.46 ± 0.43
11	15.6	330	533	371(31), 353(20), 209(100), 191(73), 179(18), 135(29)	Dicaffeoylaltraric acid isomer 3	1.05 ± 0.19
12	16.8	326	533	371(13), 353(13), 209(100), 191(85), 179(15), 135(23)	Dicaffeoylaltraric acid isomer 4	0.93 ± 0.17
13	17.1	324	559	397(40), 293(11), 235(40),191(11), 179(64), 161(96), 135(76)	4,5-di-*O*-caffeoyl-2,7-anhydro-D-glycero-*O*-β-galacto-oct-2-ulopyranosonic acid	204.26 ± 12.17
14	18.0	330	533	371(27), 353(18), 209(100), 191(79), 179(12), 135(19)	Dicaffeoylaltraric acid isomer 5	257.10 ± 41.52
15	18.6	330	533	371(48), 353(33), 209(100), 191(96), 179(21), 135(29)	Dicaffeoylaltraric acid isomer 6	136.68 ± 26.82
16	21.0	328	503	371(33), 209(7), 179 (9), 161(11)	Leeaoside [$C_{24}H_{39}O_{11}$]	3.38 ± 0.58
17	21.4	326	515	353(80), 335(34), 191(88), 179(96), 173(94), 161(67), 155(27), 135(100)	Dicaffeoylquinic acid	39.72 ± 6.14
18	22.1	330	533	371(36), 353(20), 209(100), 191(99), 179(24), 135(28)	Dicaffeoylaltraric acid isomer 7	36.23 ± 5.19
19	23.0	324	353	191(97), 179(63), 161(9), 135(100)	Caffeoylquinic acid	178.63 ± 28.03
20	25.7	326	515	353(89), 335(4), 191(85), 179(94), 173(97), 161(24), 155(3), 135(100)	Dicaffeoylquinic acid	26.96 ± 3.00
21	28.0	328	695	533(34), 515(6), 371(40), 353(35), 209(100), 191(78), 179(13), 147(8), 135(16)	Tricaffeoylatraric acid isomer 1	140.98 ± 16.98
22	28.9	330	695	533(33), 515(4), 371(30), 353(41), 209(100), 191(85), 179(22), 147(12), 135(12)	Tricaffeoylatraric acid isomer 2	3.41 ± 0.59
23	29.5	330	353	191(67), 179(85), 173(92), 161(18), 135(100)	Caffeoylquinic acid	1.17 ± 0.18
24	29.8	328	695	533(35), 515(12), 371(33), 353(52), 209(100), 191(3), 179(21),161(15), 147(9), 135(13)	Tricaffeoylatraric acid isomer 3	649.73 ± 119.40
25	32.1	328	695	533(33), 515(4), 371(44), 353(31), 209(100), 191(75), 179(15), 147(12), 135(13)	Tricaffeoylatraric acid isomer 4	27.54 ± 4.68
26	37.4	332	677	515(13), 497(20), 353(26), 335(27), 191(4), 179(22), 161(100),135(37)	Tricaffeoylquinic acid	2.96 ± 0.16
					Total:	2166.66 ± 58.59

Data are the mean ± standard deviation of three replicates.

Table 2
Retention time (Rt), wavelengths of maximum absorption in the visible region (λ_{max}), mass spectral data, tentative identification and quantification (μg/g DM) of non-anthocyanin compounds observed in mashua.

Peak	Rt (min)	λ_{max} (nm)	Molecular ion $[M-H]^-$ (m/z)	Main fragments (Da)	Tentative identification	μg/g DM
1	6.61	272	305	219 (26), 179 (17), 125 (100)	(+)-Gallocatechin	t
2	7.28	314	337	191 (100), 173 (10), 163 (69)	*p*-coumaroylquinic acid	10.99 ± 0.60
3	8.12	274	305	219 (33), 179 (20), 125 (100)	(-)-Epigallocatechin	t
4	9.40	280	203	159 (4), 142 (43)	Tryptophan	–
5	11.18	354	787	317 (100)	Myricetin rhamnosyldihexoside	15.26 ± 1.21
6	12.70	278	289	–	(-)-Epicatechin	9.22 ± 0.80
7	13.26	354	641	317 (100)	Myricetin dihexoside	1.81 ± 0.21
8	14.50	354	771	301 (100)	Quercetin rhamnosyldihexoside	3.28 ± 0.17
9	15.95	355	829	317 (100)	Myricetin acetylrhamnosyldihexoside	t
10	16.10	355	625	301 (100)	Quercetin dihexoside	t
11	16.40	358	741	609 (3), 301 (100)	Quercetin pentosyl rhamnosylhexoside	t
12	19.82	356	609	301 (100)	Quercetin 3-rutinoside	40.62 ± 0.25
13	24.27	354	623	315 (100)	Isorhamnetin 3-rutinoside	6.98 ± 0.27
					Total:	88.16 ± 3.51

t: traces.
Data are the mean ± standard deviation of three replicates.

2.4.2. Anthocyanins

Samples were analyzed in an AQUA® HPLC system (Phenomenex) equipped with a reverse phase C_{18} column (5 μm, 150 mm × 4.6 mm i.d) at 35 °C according to García-Marino et al. (2010). Detection was carried out at 520 nm. MS was performed in the same equipment described above.

Zero grade air served as the nebulizer gas (40 psi) and turbo gas (600 °C) for solvent drying (50 psi). Nitrogen served as the curtain (100 psi) and collision gas (high). Both quadrupole units were set at unit resolution. The ion spray voltage was set at 5000 V in the positive mode. EMS and ESI methods were used for acquisition of full scan spectra and fragmentation patterns of the precursor ions, respectively.

Setting parameters used for EMS mode were: declustering potential (DP) 41 V, entrance potential (EP) 7.5 V and collision energy (CE) 10 V. Parameters for EPI mode were: DP 41 V, EP 7.5 V, CE 10 V, and collision energy spread (CES) 0 V. For the quantitative analysis of anthocyanins, a calibration curve was obtained by injection of cyanidin 3-*O*-glucoside in concentration of 1–100 μg/mL (purple sweet potato, Table 5). The results were expressed in μg/g DM.

2.5. Statistical analysis

The obtaining of phenolic extracts and analysis of compounds were carried out at least in triplicate. The results were expressed as the mean ± standard deviation and significant differences were observed using the Tukey test at a probability level ($p < 0.05$), using the software IBM SPSS Statistics V22.*0*.

3. Results and discussion

3.1. Identification of phenolic compounds in Andean tubers

Identification and quantification of individual phenolic compounds of different Andean tubers (yacon, mashua, melloco and sweet potato) were carried out by HPLC-DAD-MS^n analysis. Fig. 1 shows the chromatographic profile of phenolic compounds of yacon recorded at 280 nm, as an example of the phenolic profiles observed. Tables 1–5 present the data obtained from HPLC-DAD-MS analysis (retention time, λ_{max}, pseudomolecular ions, MS^2 fragment ions, and relative abundances of fragment ions) used for the identification and quantification of phenolic compounds in the four Andean tubers.

3.1.1. Hydroxycinnamic compounds

Hydroxycinnamic acid derivatives were found in all studied Andean tubers with exception of mashua (*Tropaeolum tuberosum*). Diverse hydroxycinnamic acid derivatives were identified in yacon (*Smallantus sonchifolius),* melloco (*Ullucus tuberosus*) and purple sweet potato (*Ipomea batatas)*.

Ferulic acid (peak 8 in melloco) (Figure S2 A) was completely identified according to their retention time, mass and UV–vis characteristics by comparison with commercial standard.

Peaks 1, 2, 6, 7, 8, 19 and 23 in yacon (Fig. 1) and peaks 1, 3, 4 and 19 in purple sweet potato (Figure S3 A) showed an UV–vis spectrum similar to caffeic acid with λ_{max} 324–330 nm but eluted at different retention times. They presented a precursor ion $[M-H]^-$ at *m/z* 353 and fragments at *m/z* 191 due to the deprotonated quinic acid, 179

Table 3
Retention time (Rt), wavelengths of maximum absorption in the visible region (λ_{max}), mass spectral data, tentative identification and quantification (μg/g DM) of non-anthocyanin compounds observed in melloco.

Peak	Rt (min)	λ_{max} (nm)	Molecular ion $[M-H]^-$ (m/z)	Main fragments (Da)	Tentative identification	μg/g DM
1	10.09	330	531	193 (20)	Ferulic acid derivative	4.31 ± 0.23
2	11.83	280	203	159 (9), 142 (34)	Tryptophan	–
3	15.99	352	755	301 (100)	Quercetin dirhamnosylhexoside	0.83 ± 0.03
4	17.99	348	739	593 (7), 285 (92)	Kaempferol-*O*-rhamnoside-rutinoside	29.45 ± 2.26
5	18.41	360	769	315 (73)	Isorhamnetin-O-dirhamnosylhexoside	1.23 ± 0.02
6	19.49	350	609	301 (100)	Quercetin 3-rutinoside	2.60 ± 0.05
7	20.28	354	593	285 (100)	Kaempferol-3-rutinoside	t
8	21.03	322	193	149 (23)	Ferulic acid	1.39 ± 0.05
9	23.86	356	635	285 (100)	Kaempferol acetylrhamnosylhexoside	0.85 ± 0.05
10	24.12	330	623	315 (100)	Isorhamnetin 3-rutinoside	0.14 ± 0.01
					Total:	40.80 ± 1.95

t: traces.
Data are the mean ± standard deviation of three replicates.

Table 4
Retention time (Rt), wavelengths of maximum absorption in the visible region (λ_{max}), mass spectral data, tentative identification and quantification (μg/g DM) of non-anthocyanins compounds present in purple sweet potato.

Peak	Rt (min)	λ_{max} (nm)	Molecular ion [M-H] − (m/z)	Main fragments (Da)	Tentative identification	μg/g DM
1	5.38	326	353	191(56), 179(34), 173(4), 161(5), 135(52)	Caffeoylquinic acid isomer 1	t
2	7.70	324	465	303(100), 193(35)	Ferulic hexoside derivative	t
3	8.41	326	353	191(100),179(9), 161(23),135(22)	Caffeoylquinic acid isomer 2	32.64 ± 4.52
4	10.20	324	353	191(100),179(4), 161(19),135(10)	Caffeoylquinic acid isomer 3	5.88 ± 0.02
5	10.77	288, 338	449	449(100), 287(46)	Eriodictyol hexoside	t
6	12.12	278	203	159(7), 142(32)	Tryptophan	–
7	12.95	288, 338	449	287(33)	Eriodictyol 7-glucoside	t
8	13.69	312	337	193(8), 191(100), 173(10), 163(14), 145(5)	*p*-coumaroyl quinic acid isomer 1	t
9	14.55	314	337	193(7), 191(100), 173(2), 163(4)	*p*-coumaroyl quinic acid isomer 2	t
10	15.95	350	625	301(100)	Quercetin dihexoside	t
11	16.55	326	367	191(16), 179(88), 161(70), 135(100)	Feruloylquinic acid isomer1	1.83 ± 0.23
12	16.89	332	367	193(18), 191(17), 179(36), 161(36), 135(100)	Feruloylquinic acid isomer 2	t
13	18.41	346	609	285(48)	Kaempferol dihexoside	46.22 ± 0.07
14	19.55	326	651	285(86)	Kaempferol	12.84 ± 0.45
15	19.79	354	681	315(100)	Isorhamnetin acyldihexoside	28.46 ± 0.06
16	21.45	324	515	353(81), 335(31), 191(90), 179(100), 173(95), 161(71), 155(29),135(95)	Dicaffeoylquinic acid isomer 1	6.67 ± 0.65
17	22.19	324	515	353(39), 335(18), 191(45), 179(71), 173(86), 161(41), 155(12),135(100)	Dicaffeoylquinic acid isomer 2	t
18	22.64	324	515	353(72), 335(6), 191(91), 179(80), 173(33), 161(20), 155(4),135(100)	Dicaffeoylquinic acid isomer 3	t
19	23.08	324	353	191(92),179(100), 161(34),135(100)	Caffeoylquinic acid isomer 4	36.07 ± 4.19
20	24.87	346	447	285(69)	Kaempferol 3-glucoside	2.02 ± 0.26
21	25.88	324	515	353(59), 335(2), 191(57), 179(78), 173(100), 161(11), 155(5),135(91)	Dicaffeoylquinic acid isomer 4	2.14 ± 0.06
22	26.88	332	771	609(6), 285(100)	Kaempferol trihexoside	0.18 ± 0.02
23	27.63	318	529	367(37), 335(3), 179(7), 173(17), 161(100), 135(16)	Feruloylquinic-hexoside acid isomer 1	t
24	28.86	328	529	367(33), 355(34), 179(47), 173(19), 161(14), 135(72)	Feruloylquinic-hexoside acid isomer 2	t
25	30.64	328	529	367(67), 179(32), 173(98), 161(100), 135(48)	Feruloylquinic-hexoside acid isomer 3	t
					Total:	174.94 ± 12.54

t: traces. Data are the mean ± standard deviation of three replicates.

[caffeic acid-H]$^-$, 173 and 135, characteristics of caffeoylquinic acid according to their characteristic fragmentation pattern (Clifford et al., 2005). Similarly, peaks 17, 20 and 26 in yacon (Fig. 1) were tentatively assigned as dicaffeoylquinic (peaks 17, 20) and tricafreoylquinic acid (peak 26) (Table 1), and peaks 16–18 and 21 in purple sweet potato (Figure S3 A) were assigned as dicaffeoylquinic acid (Table 4), based on their fragmentation patterns described by Clifford et al. (2005). Peak 3 in yacon (Fig. 1) was tentatively detected as aldaric acid (glucaric acid) derivative according to its UV–vis spectra (λ_{max} 328 nm) (Table 1) and precursor ion [M − H]$^-$ at *m/z* 371 and fragment ion at *m/z* 209, corresponding to an aldaric acid residue.

Peaks 4 and 5 in yacon (Fig. 1) presented a precursor ion [M − H]$^-$ at *m/z* 397, and fragment ions at *m/z* 235 due to the loss of caffeoyl moiety, 179 [caffeoyl acid –H]$^-$ and 135 [caffeoyl acid – carboxylic group]$^-$. These compounds were tentatively identified as 4-*O*-caffeoyl-2,7-anhydro-D-glycero-β-D-galactooct-2-ulopyranosonic acid isomers (Table 1). Thus, peak 13 in yacon showed an additional caffeoyl group with respect to previous compounds (peaks 4 and 5), with [M − H]$^-$ at *m/z* 559, and fragments ions at *m/z* 397 and 235 was putatively identified as 4,5-di-*O*-caffeoyl-2,7-anhydro-D-glycero-*β*-D-galacto-oct-2-ulopyranosonic acid (Table 1). These three compounds were previously isolated in yacon (*Smallanthus sonchifolius*) and confirmed their identity by NMR (Takenaka et al., 2003).

Peaks 9–12, 14, 15 and 18 in yacon (Fig. 1) showed a precursor ion

Table 5
Retention time (Rt), wavelengths of maximum absorption in the visible region (λ_{max}), mass spectral data, tentative identification and quantification (μg/g DM) of anthocyanins compounds present in purple sweet potato.

Peak	Rt (min)	λ_{max} (nm)	Molecular ion [M-H] − (m/z)	Main fragments (Da)	Tentative identification	μg/g DM
1	9.60	514	773	611(25), 449(100), 287(88)	Cyanidin 3-dihexoside-5-hexose	13.08 ± 0.51
2	12.15	500	757	595(39), 433(67), 271(100)	Pelargonidin 3-dihexoside-5-hexoside	6.15 ± 0.31
3	18.74	520	893	731(19), 449(42), 287(31)	Cyanidin 3-*p*-hidroxybenzoldihexoside-5-hexoside	4.18 ± 0.06
4	20.31	522	935	773(21), 449(17), 287(8)	Cyanidin 3-dicafeoylhexoside-5-hexoside	3.91 ± 0.06
5	23.19	504	877	715(15), 433(46), 271(50)	Pelargonidin 3-*p*-hydroxybenzoldihexoside-5-hexoside	2.20 ± 0.04
6	24.77	506	919	757(22), 433(22), 271(33)	Pelargonidin 3-caffeoyldihexoside-5-hexoside	2.17 ± 0.05
7	25.87	522	949	787(23), 449(36), 287(40)	Cyanidin 3-feruloyldihexoside-5-hexoside	3.32 ± 0.03
8	36.57	530	935	773(37), 449(15), 287(20)	Cyanidin 3-dicafeoylhexoside-5-hexoside	44.78 ± 1.15
9	36.88	520	893	731(20), 449(33), 287(40)	Cyanidin 3-*p*-hydroxybenzoldihexoside-5-hexoside	20.28 ± 0.57
10	38.50	524	919	757(53), 433(24), 271(22)	Pelargonidin 3-caffeoyldihexoside-5-hexoside	30.84 ± 1.13
11	39.48	512	877	715(50), 433(40), 271(55)	Pelargonidin 3-*p*-hydroxybenzoldihexoside-5-hexoside	18.81 ± 0.85
12	41.25	528	933	771(20), 433(26), 271(13)	Pelargonidin 3-feruloyldihexoside-5-hexoside	7.46 ± 0.12
					Total:	157.16 ± 4.18

Data are the mean ± standard deviation of three replicates.

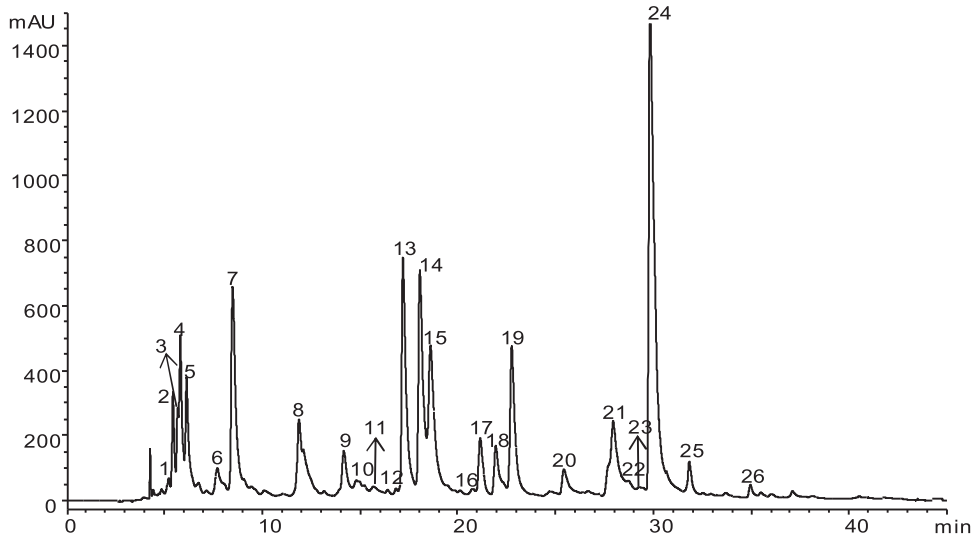

Fig. 1. Chromatographic profile of non-anthocyanin compounds observed in yacon recorded at 280 nm. Peaks assignment is exposed in Table 1.

$[M-H]^-$ at *m/z* 533, and fragments at *m/z* 371 and 209 due to losses of one and two caffeoyl moieties, respectively. These compounds were tentatively identified as dicaffeoylaltraric acid isomers (Table 1). Similarly, peaks 21, 22, 24 and 25 (Fig. 1) presented one additional caffeoyl group with respect to previous compounds, with a precursor ion $[M-H]^-$ at *m/z* 695 and fragments at *m/z* 533, 371 and 209. These compounds were tentatively identified as tricaffeoylaltraric acid isomers (Table 1).

Peak 16 in yacon (Fig. 1) showed an UV–vis spectrum similar to caffeic acid with λ_{max} 328 nm. It presented a precursor ion $[M-H]^-$ at *m/z* 503 and fragment ions at *m/z* 371 corresponding to the loss of a pentoside moiety $[M\text{-}132]^-$, at *m/z* 209 due to the losses of one pentoside and one hexoside $[M\text{-}132\text{-}162]^-$ and *m/z* 179 corresponding to caffeoyl moiety. This compound was tentatively identified as leeaoside (Table 1).

Peak 2 in mashua (Figure S1 A), and peaks 8, 9 in purple sweet potato (Figure S3) were identified as *p*-coumaroylquinic acid (Tables 2 and 4); and peaks 11 and 12 in purple sweet potato (Figure S3 B) were identified as feruloylquinic acid (Table 4). These compounds showed a pseudomolecular ion $[M-H]^-$ at *m/z* 337 and 367, and fragment ions at *m/z* 191 due to the deprotonated quinic acid, and 163 and 193 corresponding to [*p*-coumaroyl –H]− and [feruloyl –H]$^-$, respectively.

Peaks 23–25 in purple sweet potato (Figure S3 A) showed typical UV–vis spectra of ferulic acid. These compounds were identified as feruloylquinic-hexoside acid (Table 4) according to their pseudomolecular ion $[M-H]^-$ at *m/z* 529, and fragments characteristic of a feruloylquinic acid, the MS^2 spectrum of these compounds produced fragments of 367 Da ($[M\text{-}H\text{-}162]^-$, due to the loss of a hexose residue) and 355 Da ($[M\text{-}H\text{-}174]^-$, due to the loss of a moiety of quinic acid).

To sum up, chlorogenic acids, esters formed between certain trans cinnamic acids, most commonly caffeic, *p*-coumaric and ferulic acid and quinic acid (Clifford et al., 2003, 2005; Clifford et al., 2006, 2007) were found in yacon and purple sweet potato.

The presence of caffeoyl derivatives in the yacon variety analyzed in our study was in agreement with the previous studies carried out by UPLC-ESI-Q-TOF-MS^n in yacon coming from Brazil (Gomes da Silva et al., 2018). The presence of ferulic and caffeic acid in yacon (*S. sonchifolius*, var. INIAP-ECU-1247) has been also reported in yacon coming from Ecuador (*S. sonchifolius*, Asteraceae), cultivated in the Czech Republic and analyzed by HPLC-MS (Simonovska et al., 2003).

The presence of ferulic and quinic acid in purple sweet potato (*I. batatas,* var. INIAP-ECU-morado) has also been observed in five varieties of purple sweet potato grown in China (Wang et al., 2018).

In mashua cultivated in Peru, Chirinos et al. (2008a) also observed the presence of *p*-coumaroylquinic acid but they did not find feruloylquinic acid, as observed in the present study for mashua (*Tropaeolum tuberosum*, var. INIAP-ECU-Izaño). The differences between the type and content of phenolic compounds identified can be due to the cultivar and growing conditions, type of solvent, pH value, the water-solvent ratio and extraction time (Chirinos et al., 2007).

3.1.2. Flavan-3-ols

Flavan-3-ols monomers were only identified in mashua sample. (+)-Gallocatechin (peak 1), (-)-epigallocatech (peak 3) and (-)-epicatechin (peak 6) (Figure S1 A) were identified according to their retention time and mass and UV–vis characteristics by comparison with commercial standards (Table 2).

These results are related to those obtained by Chirinos et al. (2008a), who characterized non-anthocyanin phenolic compounds in Peruvian mashua genotypes by HPLC-DAD, revealing the presence of gallocatechin, procyanidin B2, epigallocatechin and (-)-epicatechin.

3.1.3. Flavonols

Flavonols were the main flavonoids detected in all studied samples with the exception of yacon sample, being quercetin, kaempferol, myricetin and isorhamnetin derivatives found mostly in mashua, melloco and purple sweet potato.

Quercetin 3-rutinoside and isorhamnetin 3-rutinoside were found in mashua and melloco samples (Tables 2 and 3), while kaempferol 3-rutinoside was only found melloco and kaempferol 3-glucoside was only found in purple sweet potato (Table 4). These compounds were positively identified according to their retention time and mass and UV–vis characteristics by comparison with commercial standards.

Myricetin derivatives (peaks 5, 7 and 9) (Figure S1 B) were only identified in mashua sample. These compounds presented similar UV–vis spectra to myricetin glycoside and fragment ion at *m/z* 317. Myricetin rhamnosyl-dihexoside (peak 5) ($[M-H]^-$ at *m/z* 787), myricetin dihexoside (peak 7) ($[M-H]^-$ at *m/z* 641) and myricetin acetylrhamnosyl-dihexoside (peak 9) ($[M-H]^-$ at *m/z* 829) released fragments corresponding to the losses of rhamnosyl moiety (-146 amu), two hexosides units (-324 amu) and acetyl residue (-42 amu). In none of them the identity of the sugar and positions of location of the substituents could be established.

Other quercetin derivatives were peaks 8, 10 and 11 in mashua (Figure S1 B) and peak 3 in melloco (Figure S2 B). These compounds were assigned to a quercetin rhamnosyldihexoside ($[M-H]^-$ at *m/z* 771) (peak 8), quercetin dihexoside ($[M-H]^-$ at *m/z* 625) (peak 10), quercetin pentosyl rhamnosylhexoside ($[M-H]^-$ at *m/z* 741) (peak 11)

(peak 3 in melloco), quercetin dirhamnosylhexoside ($[M-H]^-$ at *m/z* 755), according to their precursor ions and MS^2 spectra, releasing fragments corresponding to the losses of rhamnosyl moieties (-146 amu), two hexosides units (-324 amu) and one pentosyl residue (-132 amu). In none of them the identity of the sugar and positions of location of the substituents could be established.

Kaempferol derivatives (λ_{max} around 347 nm, and unique fragment ion at *m/z* 285) were also identified in melloco and purple sweet potato. kaempferol-*O*-rhamnoside-rutinoside (peak 4) was identified in melloco (Figure S2 B, Table 3), showing precursor ions $[M-H]^-$ at *m/z* 739 and fragment ions at *m/z* 593 ($[M\text{-}146]^-$, loss of a rhamnoside moiety) and at *m/z* 285 ($[M\text{-}308]^-$, loss of a rhamnoside-hexoside moiety). A kaempferol acetylrhamnosylhexoside (peak 9) was also detected in melloco (Figure S2 B, Table 3), showing precursor ions $[M-H]^-$ at *m/z* 635, releasing MS^2 fragment at *m/z* 285 ($[M\text{-}42\text{-}146\text{-}162]^-$, loss of acetyl + rhamnosyl-hexoside residue).

Kaempferol dihexoside (peak 13), kaempferol acetyldihexoside (peak 14) and kaempferol trihexoside (peak 22) were tentatively identified in purple sweet potato (Figure S3 A, Table 4). These compounds were identified according to $[M-H]^-$ at *m/z* 609, 651 and 771, respectively. Fragment ion at *m/z* 285 corresponded to kaempferol due to losses of 324 amu (two hexoside units), loss of 42 amu (one acetyl residue) and 486 (three hexoside units).

Another group of detected flavonols were isorhamnetin derivatives according to their UV–vis and mass spectra. All of them released a fragment ion at *m/z* 315 and they were tentatively identified in melloco (peak 10) (Figure S2 B, Table 3) and sweet purple potato (peak 15) (Figure S3 A, Table 4). The first peak was positively identified as isorhamnetin 3-rutinoside by comparison with standard, while peak 15 in sweet purple potato was assigned to isorhamnetin acetyldihexoside from the loss of 366 amu (-42-324 amu, corresponding to acetyl + dihexosyl residues).

The Ecuadorian yacon var. INIAP-ECU-1247 analyzed in the present study differs from the Ecuadorian yacon var. Asteraceae analyzed by Simonovska et al. (2003) by the presence of quercetin.

Purple sweet potato var. INIAP-ECU-purple presented kaempferol and isorhamnetin derivatives as the main flavonols; compounds not observed in five varieties of purple sweet potato grown in China, which had only shown the presence of *O*-hexoside of quercetin as flavonol compound (Wang et al., 2018).

To the best of our knowledge, the presence of flavonols had not been reported for mashua or melloco so far.

3.1.4. Flavanones

This flavonoid group was only identified in purple sweet potato. Peak 7 (Figure S3) was identified as eriodyctiol 7-glucoside (Table 4) by comparison with a commercial standard. Peak 5 (Figure S3) was assigned to eriodyctiol hexoside (Table 4) according to its $[M-H]^-$ at 449 and fragment ion corresponding to the loss of hexosyl moiety (-162 amu). This type of compound has not been reported for purple sweet potato in previous studies.

3.1.5. Anthocyanins

Twelve anthocyanin pigments were only detected in purple sweet potato sample (Table 5). Pigments were cyaniding (Cy) and pelargonidin (Pg) derivatives, as demonstrated for their UV–vis spectra and mass spectral data.

Peaks 1 and 2 (Figure S3) corresponded to derivatives of cyanidin and pelargonidin. Peak 1 showed an UV–vis spectra λ_{max} 514 nm and precursor ion at *m/z* 773, releasing a fragment ions at *m/z* 611 ($[M\text{-}162]^+$ due to the loss of a hexoside moiety, at *m/z* 449 ($[M\text{-}162\text{-}162]^+$ derived from the losses of two successive hexoside moieties, and 287 $([M\text{-}162\text{-}162\text{-}162])^+$ corresponding to cyanidin. This peak was tentatively identified as cyanidin 3-dihexoside-5-hexoside. Similarly, peak 2 presented the same fragmentation pattern as peak 1, which was tentatively assigned as pelargonidin 3-dihexoside-5-hexoside, based on the fragment ion at *m/z* 271 corresponding to pelargonidin.

Peaks 3–12 (Figure S3 B) corresponded to acyl derivatives of cyanidin and pelargonidin. Peaks 3 and 9 showed the molecular ions at *m/z* 893 that release three fragments MS^2 at *m/z* 731, (-162 amu, loss of one hexoside moiety), *m/z* 449 (-162-120 amu, loss of hexoside-p-hydroxybenzoyl moieties), *m/z* 287 (cyanidin) corresponded to cyanidin-3-*p*-hydroxybenzoylhexoside-5-hexoside (peak 3) and cyanidin-3-*p*-hydroxybenzoyldihexoside-5-hexoside (peak 9).

Peaks 5 and 11 showed a similar fragmentation pattern, so that it can be assigned to pelargonidin-3-*p*-hydroxybenzoylhexoside-5-hexoside (peak 5) and pelargonidin-3-*p*-hydroxybenzoyldihexoside-5-hexoside (peak 11).

Peaks 4, 6, 8 and 10 were observed around λ_{max} 506–530 nm, with a UV–vis spectra characteristic of acyl anthocyanin derivatives. These compounds presented precursor ions at *m/z* 935 and 919, releasing three pairs of fragment ions at *m/z* 773 and 757 ($[M\text{-}162]^+$ due to the loss of a hexoside moiety), *m/z* 499 and 433 ($[M\text{-}162\text{-}162]^+$ due to the loss of a caffeoyl + hexoside residues), and *m/z* 287 (cyanidin) and 271 (pelargonidin) corresponding to cyanidin 3-dicafeoylhexoside-5-hexoside (peaks 4 and 8), and pelargonidin-3-caffeoyldihexoside-5-hexoside (peaks 6 and 10).

Peaks 7 and 12 showed their maximum absorption to λ_{max} 522 and 528 nm, respectively, with a UV–vis spectra characteristic of acyl anthocyanin derivatives. These compounds had precursor ions at *m/z* 949 and 933, releasing three fragment ions at *m/z* 787 and 771 ($[M\text{-}162]^+$ due to the loss of a hexoside moiety), *m/z* 499 and 433 ($[M\text{-}162\text{-}176]^+$ due to the loss of a feruloyl + hexoside residues), and *m/z* 287 (cyanidin) and 271 (pelargonidin) corresponded to cyanidin-3-feruloyldihexoside-5-hexoside (peak 7) and pelargonidin-3-feruloyldihexoside-5-hexoside (peak 12).

The presence of anthocyanins has been reported in different varieties of purple sweet potato (Gras et al., 2017; Wang et al., 2018; Sun et al., 2018). Cyanidin derivatives have also been observed in some varieties of purple sweet potato grown in Japan, which also showed presence of peonidin (Cuevas Montilla et al., 2011).

3.1.6. Others non-phenolic compounds

Tryptophan, an aromatic amino acid was found in mashua (peak 4) (Figure S1 A), melloco (peak 2) (Figure S2 B) and purple sweet potato (peak 6) (Figure S3). This compound showed a pseudomolecular ion $[M-H]^-$ at *m/z* 203. Its identity was confirmed by comparison with retention time and UV–vis characteristics with commercial standard.

The detection of this amino acid in mashua is in accordance with the observed by Grau et al. (2003); while in melloco and purple sweet potato, tryptophan had not been reported so far.

3.2. Content of phenolic compounds in Andean tubers

Table 6 shows the total content of phenolic compounds identified. These values were obtained, by adding the concentrations reported in the Tables 1–5, for each tuber. According to this, yacon has a very high phenolic content followed by purple sweet potato, whereas mashua and melloco exhibited the lowest phenolic content ($p < 0.05$).

Fig. 2 shows the contribution of each phenolic group with respect to

Table 6
Total content of phenolic compounds identified (μg/g DM) by HPLC–DAD–ESI/MS^n in Andean tubers.

Tuber	Total
Yacon	2166.66 ± 58.59 d
Mashua	88.16 ± 3.51 ab
Melloco	40.80 ± 1.95 a
Purple sweet potato	332.10 ± 8.36 c

DM: dry matter. Means with different letters a–d denote significant difference ($p < 0.05$) in the same column.

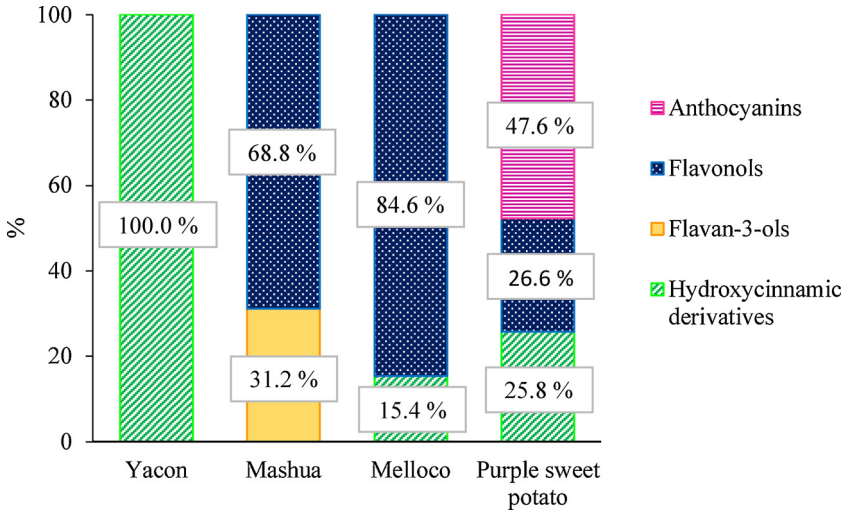

Fig. 2. Percentage of distribution of different phenolic groups with respect to the total phenolic content.

the total of phenolic compounds detected by HPLC–DAD–ESI/MS^n in the Andean tubers analyzed. Thus, 100% of phenolic compounds present in yacon correspond to hydroxycinnamic derivatives, while in melloco and purple sweet potato only 15.4 and 25.8% of phenolic compounds are constituted by this type of compounds. Melloco, instead, showed the greatest presence of flavonols equivalent to 84.6%, also present in mashua and purple sweet potato but in a proportion of 68.8 and 26.6%, respectively. Flavan-3-ols were detected only in mashua (31.2% of total phenolic compounds), and anthocyanins were only present in purple sweet potato in a proportion of 47.6%.

Hydroxycinnamic acid derivatives and flavanoids (eg. flavonols, flavanols and anthocyanins) have exerted anti-proliferative activities in numerous cancer cell lines and inhibited tumour growth in some animal models (Roleira et al., 2015).

3.2.1. Non-anthocyanin compounds

Yacon showed mainly hydroxycinnamic quinic acid derivatives in a total concentration of 2166.66 μg/g DM (Table 1). Chlorogenic acids observed are hydroxycinnamic esters (isomers of quinic acid), that can reduce the risk of developing metabolic syndrome by reducing the risk of type 2 diabetes and decreasing triglyceride concentrations. These effects of chlorogenic acid consumption have been attributed to its antioxidant and anti-inflammatory properties (Tajik et al., 2017).

The phenolic total concentration in mashua (88.16 μg/g DM) was constituted by quercetin 3-rutinoside as the most abundant compound (40.62 μg/g DM) (Table 2). This glycoside has shown effective protection against mortality induced by radiation in animal models, related to the inhibition of oxidative stress and apoptosis (Bansal et al., 2012).

The total phenolic content observed in melloco (40.8 μg/g DM) was constituted by kaempferol-*O*-rhamnoside-*O*-rutinoside as the most abundant phenolic compound (29.45 μg/g DM) followed by ferulic acid derivative (4.31 μg/g DM), and quercetin rutinoside (2.60 μg/g DM) (Table 3). This polyphenol has exerted anti-inflammatory and anti-asthmatic effects in mice model (Chung et al., 2015). Ferulic acid in recent years have been deeply studied due to its preventive effect against cancer, cardiovascular diseases, diabetes mellitus, skin disease and Alzheimer's disease (Shahabadi et al., 2017; Sgarbossa et al., 2015); whist quercetin 3-*O*-rutinoside has shown protective effect against atherosclerosis, oxidative stress, cardiotoxicity, endothelial cell dysfunction and heart failure (Patel et al., 2018). However, it has been mentioned that very few plants have the ability to store rutin in great quantities (Habtemariam and Varghese, 2015).

The analysis by HPLC–DAD–ESI/MS^n applied on purple sweet potato samples, allowed to identify 25 peaks of non-anthocyanin compounds, constituted by flavonols and total hydroxycinnamic acid derivatives, almost in similar proportion (89.72 *vs.* 85.23 μg/g DM), resulting a total of 174.95 μg/g DM (Table 4). The most abundant compounds were caffeoylquinic acids, kaempferol dihexoside, isorhamnetin, and kaempferol acetyldihexoside. Caffeoylquinic acids and di-caffeoylquinic acids are the main derivatives of chlorogenic acid, which is found in plant extracts (eg., coffee). Chlorogenic acid derivatives reduces the risk of cardiovascular disease and type 2 diabetes mellitus (Ranheim, and Halvorsen, 2005; Salazar-Martinez et al., 2004), antibacterial activity (Almeida et al., 2006) and anti-inflammatory effects (Santos et al., 2006), as mentioned in previous lines.

3.2.2. Anthocyanins

Anthocyanin compounds were observed only in purple sweet potato, in a concentration of 157.16 μg/g DM, being the most abundant compounds cyanidin 3-dicafeoyldihexoside-5-hexoside, followed by pelargonidin 3-caffeoyldihexoside-5-hexoside, and cyanidin 3-p-hydroxybenzoildihexoside-5-hexoside (Table 5).

The type and concentration of anthocyanin compounds not only provides information on their antioxidant potential, but also gives an idea on the color of the vegetable pulp. In the case of the purple sweet potato, when the ratio peonidin/cyanidin is superior to 1 the color turns to red, and when the ratio peonidin/cyanidin is inferior to 1, the color turns to blue (Cuevas Montilla et al., 2011).

The absence of peonidin in the sweet potato analyzed and the presence of cyanidin (peonidin/cianidin < 1), indicates a pulp of intense blue color, in accordance with the levels observed in the analyzed samples.

4. Conclusion

The phenolic composition of four undervalued Andean tubers from Ecuador, i.e., yacon, mashua, melloco and purple sweet potato, were analysed by HPLC-DAD-ESI/MS^n. Notable qualitative and quantitative differences were observed among them, due to genetic differences and/or origin of the crop. The identification of phenolic compounds has been described for the first time in these Andean tubers. Non-flavonoid compounds, such as hydroxycinnamic derivatives were identified in yacon, purple sweet potato samples and melloco, accounting for 100%, 26%, 15% of the total of phenolic compounds, respectively, being yacon the tuber with the highest total phenolic content. The presence of flavonoid, such as flavan-3-ols, was only shown in mashua sample, accounting for 31% of the total of phenolic compounds. Flavonols were the most abundant group in mashua and melloco, presenting 69% and 85% of total of phenolic compounds. Purple sweet potato also showed the unique presence of anthocyanins (157.16 μg/g DM). The phenolic

profiles and phenolic content observed, especially in yacon and in purple sweet potato, point out their great potential as novel raw materials, for antioxidant compound sources of known therapeutic activity and, therefore, of great importance for health care, with promising perspectives to be used in the pharmacological field and/or in the development of new functional foods.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfca.2019.103258.

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