Phenolic compounds extracted by acidic aqueous ethanol from berries and leaves of different berry plants

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Abstract

Phenolic compounds of berries and leaves of thirteen various plant species were extracted with aqueous ethanol and analyzed with HPLC-DAD, HPLC-MS, and NMR. The total content of phenolics was consistently higher in leaves than in berries (25-7856 vs. 28-711 mg/100 g fresh weight). Sea buckthorn leaves were richest in phenolic compounds (7856 mg/100g f.w.) with ellagitannins as the dominant compound class. Sea buckthorn berries contained mostly isorhamnetin glycosides, whereas quercetin glycosides were typically abundant in most samples investigated. Anthocyanins formed the dominating group of phenolics in most dark-colored berries but phenolic acid derivatives were equally abundant in saskatoon and chokeberry berries. Caffeoylquinic acids constituted 80% of the total phenolic content (1664 mg/100g f.w.) in bilberry leaves. B-type procyanidins and caffeoylquinic acids were the major phenolic compounds in hawthorn and rowanberry, respectively. Use of leaves of some species with prunasin, tyramine and *β*-*p*-arbutin, may be limited in food applications.

Keywords: Aromatic compounds, berries, ethanol extracts, leaves, phenolic compounds

1. Introduction

Phenolic compounds are a large group of phytochemicals, existing ubiquitously in plants as secondary metabolites. In human diet, the majority of them belong to phenolic acids, flavonoids, and tannins. Besides contribution to sensory properties of food, phenolic compounds also exhibit a wide range of biological and physiological functions, such as anti-allergenic, anti-inflammatory, anti-microbial and antioxidant activities, which are beneficial for human health (Shahidi, & Naczk, 2004; Claudine, Andrzej, & Augustin, 2005; Middleton, Kandaswami, & Theoharis, 2000; Balasundram, Sundram, & Samman, 2006).

It is widely recognized that berries are rich in phenolic compounds. In addition to flavonols commonly found in berries, proanthocyanidins are the main phenolic compounds in hawthorn (*Crataegus spp.*), and anthocyanins are dominant in dark-skinned berries, such as black currant (*Ribes nigrum*) and bilberry (*Vaccinium myrtillus*) (Liu, Yang, & Kallio, 2010; Vagiri, Ekholm, Öberg, Johansson, Andersson, & Rumpunen, 2013; Govindaraghavan, 2014). Some phenolic acids (ferulic acid and *p*-coumaric acid), usually linked to lignins or other cell wall components, are also abundant in berries (Andreasen, Landbo, Christensen, Hansen, & Meyer, 2001). Owing to high contents of these compounds, berries have received more and more attention in recent years as a component of healthy diet. Some previous studies have also shown that leaves of some berry plants might be a potential source for phenolic compounds (Hokkanen, Mattila, Jaakola, Pirttila, & Ari Tolonen, 2009; Liu, Kallio, & Yang, 2011). Nettle leaves have been used as food for decades. Both black currant and sea buckthorn leaves have been used in different foods such as tea. According to Novel Food Catalogue in European commission, the application of leaves of some berry plants, such as cowberry, lingonberry, bilberry, and rowan berry have been authorized as food supplements. Therefore,

it is essential to reveal systematic knowledge on the profile and content of phenolics in leaves and berries of various wild and cultivated berry plants in order to evaluate their potential as raw materials of food, food supplements and health care products.

However, most of the data published so far have been limited to either berries or leaves of selected species, and usually have focused on specific groups of phenolic compounds. Furthermore, the extraction methods used for analytical purposes have not been applicable for food industry. In our previous study, 70% aqueous ethanol acidified with 1% acetic acid showed potential in food industry applications (unpublished results) with high efficiency for extracting phenolic compounds from berries and leaves. This standardized method was used to extract phenolic compounds from berries and leaves of wild and cultivated berry species commonly used in Northern Europe. The content and profile of phenolic compounds extracted from these berries and leaves were thoroughly investigated using high performance liquid chromatography (HPLC), mass spectrometry (MS), and nuclear magnetic resonance spectroscopy (NMR). For comparison, we also included samples of nettle (*Urtica dioica*) leaf, which has been consumed as food in Europe. This study provides important compositional information, assisting the evaluation of the potential of the raw materials for functional ingredients for food and nutraceuticals.

2. Materials and Method

2.1 Plant materials

Twenty-nine samples of berries, leaves and branches, were collected in Finland during the summer of 2013 and 2014. The berries were harvested optimally ripe based on color, flavor, and structure. Two sample of press cake were the residues after juice pressing, provided by Marjajaloste Meritalo Oy (Ylönkylä, Finland). All samples were kept at -20 °C till analyzed

(**Table 1**).

2.2 Chemicals

Reference compounds of flavonol glycosides were purchased from Extrasynthese (Genay, France), including quercetin, quercetin 3-*O*-rutinoside, quercetin 3-*O*-galactoside, quercetin 3-*O*-glucoside, quercetin 3-*O*-glucuronide, quercetin 3-*O*-(6"-malonyl)-glucoside, myricetin, myricetin 3-*O*-galactoside, myricetin 3-*O*-glucoside, kaempferol, kaempferol 3-*O*-rutinoside, kaempferol 3-*O*-glucoside, kaempferol 3-*O*-glucuronide, isorhamnetin 3-*O*-rutinoside, isorhamnetin 3-*O*-glucoside, syringetin 3-*O*-glucoside, (+)-catechin, (-)-epicatechin, cyanidin 3-*O*-rutinoside, cyanidin 3-*O*-galactoside, cyanidin 3-*O*-glucoside, cyanidin 3-*O*-arabinoside, delphinidin 3-*O*-glucoside, and malvidin 3-*O*-glucoside. 5-*O*-, 3-*O*-, and 4-*O*-caffeoylquinic acids, tyramine hydrochloride and 3-(trimethylsilyl) propionic-2,2,3,3-d_4 acid sodium salt (TSP, 98% D) were purchased from Sigma-Aldrich Co. (St. Louis, USA). B-type procyanidin dimer was prepared by the Department of Chemistry, University of Turku. Deuterium oxide (D_2O, 99.96 % D) and methanol-d_4 (CD_3OD, 99.80 % D) were from VWR International BVBA (Leuven, Belgium). Ethanol (99.5%, weight) was from ALTIA Oy (Rajamäki, Finland). Other HPLC and MS grade chemicals, such as ethyl acetate, methanol, acetonitrile, formic acid and acetic acid, were purchased from VWR International Oy (Espoo, Finland).

2.3 Extraction of phenolic compounds

Fresh plant materials were ground into powder in liquid nitrogen. Each powdered sample (4 g) was extracted using acidic aqueous ethanol (ethanol:water:acetic acid, 70:30:1, v/v/v) with a solid : solvent ratio of 1:10 (w/v, on a fresh weight basis). Ultra-sonication for 30 min and mechanical shaking for 20 min were used to assist the extraction at room temperature, which were followed by centrifugation at 4420 × *g* for 10 min. The supernatant was collected and

filtered through a 0.45 µm filter before analysis.

2.4 Full-scan analysis of raw extracts with NMR

An aliquot of 1.8 mL from each extract was lyophilized and dissolved in 600 µL solvent consisting of methanol-d_4:D_2O:TSP (8:2:0.05, v/v/w). Each sample was filtered through a 0.45 µm PTFE filter.

^{1}H NMR analyses were performed on a Bruker Avance 500 spectrometer operating at 500.13 MHz and equipped with a broadband inverse auto-tune probe (BBI-5 mm-Zgrad-ATM). The solvent-suppressed ^{1}H NMR spectra were acquired at 25 °C using a double pre-saturation (typically for residual hydroxyl and methanol signals) pulse program (Bruker's pulse program lc1pnf2), with 256 scans, an acquisition time of 3.28 s, and with spectral width of 10 kHz consisting of 64 k data points. The relaxation delay was extended to 11.70 s in these analyses to provide altogether 15 s between the pulses and to let TSP fully relax (pulse angle 30°). In addition, a set of one- and two-dimensional NMR experiments (^{13}C, 1D TOCSY, DQF-COSY, HSQC and HMBC) was performed for selected plant extracts (saskatoon leaves, saskatoon branch, chokeberry leaves, white currant leaves, red currant leaves, lingonberry berry, lingonberry leaves and cranberry press cake) to study their components in more detail.

NMR spectra were processed with TopSpin 3.2 software. The chemical shifts were referenced to the internal standard TSP at 0.00 ppm, and the phase and baseline were manually corrected.

2.5 Identification of phenolic compounds using UPLC-DAD-ESI-MS

Chromatographic-mass spectrometric analyses of the extracts were performed on a Waters

Acquity Ultra performance liquid chromatography (UPLC) system equipped with 2996 DAD detector and a Waters Quattro Premier mass spectrometer (Waters Corp., Milford, MA) with an electrospray ionization interface. A Phenomenex Aeris peptide XB-C18 column (150 × 4.60 mm, 3.6 µm, Torrance, CA) was used in chromatographic separation at a flow rate of 1.0 mL/min with a sample injection volume of 10 µL.

The mobile phase was a combination of water (A) and acetonitrile (B), both containing 5.0% (v/v) formic acid. For analysis of anthocyanins, the following gradient program was used: 0–5 min with 5–10% solvent B, 5–10 min with 10% solvent B, 10–25 min with 10–40% B, 25–30 min with 40–90% B, 30–35 min with 90–5% B. The column temperature was 36 °C, and the peaks were recorded at 520 nm. For analysis of other phenolic compounds in berry extracts, the gradient was: 0–5 min with 7% solvent B, 5–10 min with 7–12% B, 10–15 min with 12–15% B, 15–20 min with 15–20% B, 20–30 min with 20–45% B, 30–35 min with 45–7% B. The column temperature was 36 °C. The gradient for analysis of the leaf and branch extracts was: 0–15 min with 7–10% solvent B, 15–20 min with 10–13% B, 20–30 min with 13–15% B, 30–35 min with 15–25% B, 35–40 min with 25–35% B, 40–45 min with 35–60% B, 45–50 min with 60–7% B. The column was kept at room temperature. The chromatograms were recorded at three different wavelengths (280 nm for all phenolic compounds, 320 nm for phenolic acids, and 360 nm for flavonol glycosides).

In the ESI-MS system, the source temperature and the desolvation temperature were 120 °C and 300 °C, respectively. Capillary voltage, cone voltage and extractor voltage were set to 3.5 kV, 35 V, and 7 V, respectively, for negative ion mode and 4.0 kV, 22 V, and 3 V for positive ion mode. The mass range scanned was from 100 to 1000 *m/z*. The collision energy and cone voltage for MS^2 were 30 V and 22 V, respectively. The MS data analysis was

177 performed by Masslynx 4.1 software (Waters Corp., Milford, MA).

178

179 2.6 Isolation of unknown compounds using preparative HPLC and identification with NMR

180 Four peaks of unknown compounds, two from the extracts of saskatoon (*Amelanchier*
181 *alnifolia*) leaves, one from saskatoon berry and one from raspberry (*Rubus idaeus*) leaves
182 were selected for further purification and identification, due to their MS profiles and high
183 abundance in the raw extracts. The powder of 4 g leaf samples and 20 g berry sample were
184 extracted with 2 × 40 mL ethyl acetate, following the same procedure as described in **2.3**. The
185 supernatants from two extractions were combined, and the solvent was evaporated at 65°C.
186 The residue was dissolved into 2 mL of ethyl acetate and filtered through a 0.45 µm filter for
187 separation with semi-preparative HPLC.

188

189 Semi-preparative HPLC separation was performed with a Shimadzu LC-20AB liquid
190 chromatograph, consisting of a SIL-20A auto sampler, a SPD-20A UV/VIS detector, a CTO-
191 10AC column oven and a FRC-10A fraction collector (Shimadzu Corp., Kyoto, Japan). A
192 Phenomenex aeris peptide XB-C18 column (250 × 10 mm, 5 µm, Torrance, CA, USA) was
193 used. The injection volume was 100 µL. The flow rate of the mobile phase was 3 mL/min.
194 The mobile phase and other chromatographic conditions were the same as described in the
195 UPLC-DAD-ESI-MS analysis. The collected fractions were lyophilized to a powder form
196 using a VirTis AdVantage and AdVangtage Plus freeze dryer (SP SCIENTIFIC Corp., PA,
197 USA).

198

199 ^{1}H and ^{13}C NMR spectra together with variety of 2D experiments were measured with the
200 same spectrometer as described in 2.4 in methanol-d_4 and calibrated on the solvent residual
201 signal at 3.31 ppm for ^{1}H and 49.15 ppm for ^{13}C.

202

203 2.7 Quantification of phenolic compounds using HPLC-DAD

204 The quantitative analysis was performed using Shimadzu LC-10AT liquid chromatograph
205 system, coupled with a SPD-M20A VP photodiode array detector (DAD), a SIL-10A auto
206 injector, a CTO-10A column oven and a SCL-10A VP system controller (Shimadzu Corp.,
207 Kyoto, Japan). The chromatographic conditions were the same as in the UPLC-DAD-ESI-MS
208 analysis. An external standard method was used for the quantitative analysis. 1~2 mg of each
209 reference compound was dissolved in 10 mL ethanol, and diluted to four different
210 concentrations. The calibration curves were constructed by plotting the peak areas in the
211 HPLC-DAD chromatogram as a function of the concentrations. Some compounds without
212 corresponding standards were quantified by calibration curves of those standards which had
213 close to similar chemical structures.

214

215 Analyses were performed in quadruplicates. The contents of phenolic compounds were
216 expressed as the mean values and standard deviations on fresh weight basis. Data correlation
217 analysis was performed using Microsoft Excel program. For each sample, the total
218 concentration of phenolics was calculated as the sum of contents of phenolic compounds
219 identified.

220

221 **3. Results and Discussion**

222 Phenolic compounds in aqueous ethanol extracts of berries, berry press cakes, leaves, and
223 branches were identified based on analyses with UPLC-MS and NMR. The NMR spectra are
224 presented in **Supplemental Figure 1** and HPLC chromatograms of some extracts in
225 **Supplemental Figure 2**.

226

As shown in **Table 3**, 27 compounds were identified based on UV-VIS spectra, mass spectra and reference compounds and 93 compounds on the spectra and literature data. In addition, 34 compounds were tentatively identified based on UV-VIS and MS analyses only. Six unknown compounds, not identified with UPLC-MS, were identified with NMR analyses after purification with preparative HPLC and the characteristics of NMR spectra and the structures are presented in **Figure 1**.

All together 160 compounds were identified or preliminarily identified mainly including flavan-3-ols, proanthocyanidins, ellagitannins, phenolic acids derivatives, glycosylated flavonols and anthocyanins.

3.1 Phenolic compounds in berries analyzed by HPLC-DAD

Lingonberry. As shown in **Figure 2a**, 1-*O*-benzoyl-*β*-glucose (BA-Glu) accounted for 41% of the total content of phenolics (Tot-Ph) in the lingonberry extract. The identification, reported earlier by Heimhuber, Wraya, Galensab, & Herrmann (1990), was based on the NMR and MS analyses (**Figure 1b and Table 3**). Flavan-3-ols were the second most abundant group of phenolic compounds representing 25% of in lingonberries, including (+)-catechin ((+)-Cat, 22%) and (-)-epicatechin ((-)-Epic, 3%). Anthocyanins, practically all cyanidin glycosides, added up to 11% of Tot-Ph. B-type procyanidin dimers (B-PC di) and A-type procyanidin trimers (A-PC tri) together accounted for 9% of Tot-Ph. Flavonol glycosides and hydroxycinnamic acid derivatives (3-*O*-caffeoylquinic acid, 3-CQA and a ferulic acid-hexoside, FA-Hex) were present at roughly equal abundance.

Bilberry. Flavonol glycosides and anthocyanins were the only two groups of phenolic compounds found in bilberries (**Tables 3**, **Figure 2b**). Bilberry contained anthocyanins of all five anthocyanidins, accounting for 95% of Tot-Ph. Glycosides of cyanidin and delphinidin were the major compounds, followed by those of malvidin, petunidin, and peonidin (**Supplemental Table 1**). Previous research on Slovenian bilberry anthocyanins reported that the glycosides of delphinidin, cyanidins, malvidin, petunidin and peonidin represented 57.6%, 23.7%, 14.1%, 3.3%, and 1.3%, of total anthocyanins, respectively (Veberic, Slatnar, Bizjak, Stampar, & Mikulic-Petkovsek, 2015). Flavonol glycosides represented the rest of the phenolic compounds quantified including myricetin 3-*O*-glucuronide (M-Gluc), myricetin 3-*O*-galactoside (M-Gal), and myricetin 3-*O*-glucoside (M-Glu). From wild bilberries growing at the different locations, Mikulic-Petkovsek and coworkers quantified several derivatives of hydroxycinnamic acid, mostly as derivatives of coumaric acid and caffeic acid; however, none of them could be identified in our samples, likely due to the suppression of the MS spectra by the presence of anthocyanins (Mikulic-Petkovsek, Schmitzer, Slatnar, Stampar & Veberic, 2015).

Currants. White and red currants, both belonging to the species of *R. rubrum*, had the lowest Tot-Ph among the samples analyzed with levels around 30 mg/100 g fresh berries. As shown in **Tables 3**, **Figure 2c&2d**, **and Supplemental Figure 2**, the dominant compounds were phenolic acid derivatives, consisting of caffeic acid-hexosides (CaA-Hex), coumaroylquinic acid-hexosides (CoA-Hex), and vanillic acid-hexoside (VA-Hex). These compounds added up to 36% of Tot-Ph in red currants and 47% in white currants. Cyanidin glycosides represented 20% of Tot-Ph in red currants, whereas white and green currants contained no anthocyanins. Glycosylated flavonols accounted only for around 10% of total phenolic compounds in white and red currants. Phenolic acid derivatives accounted for over half of Tot-Ph in the green

currant with caffeic acid-hexosides, coumaroylquinic acid-hexosides and vanillic acid-hexoside as the major compounds (**Table 3**, **Figure 2e**). (+)-Catechin was the dominating flavan-3-ol, and (-)-epicatechin the minor one. Quercetin was the major primary flavonol in green currant, mostly as 3-*O*-rutinoside (Q-Rut), 3-*O*-glucoside (Q-Glu), and 3-*O*-(6"-malonyl)-glucoside (Q-maGlu). As the most dominating phenolic compounds (close to 90% of Tot-Ph) in black currant press cake (**Figure 2f**), the anthocyanins mainly included delphinidin 3-*O*-rutinoside (De-Rut, 32% of Tot-Ph), delphinidin 3-*O*-glucoside (De-Glu, 22%), cyanidin 3-*O*-rutinoside (Cy-Rut, 26%) and cyanidin 3-*O*-glucoside (Cy-Glu, 6%). Trace quantities were found of cyanidin 3-*O*-(6"-coumaroyl)-glucoside (Cy-coGlu) and delphinidin 3-*O*-(6"-coumaroyl)-glucoside (De-coGlu). The rest were phenolic acids (mainly as *p*-coumaric acid. *p*-CoA) and flavonol glycosides (quercetin and myricetin derivatives).

Hawthorn fruits. Flavan-3-ols and procyanidins formed the dominating fraction (75%) of phenolic compounds in hawthorn (**Supplemental Figure 2)**. (-)-Epicatechin was present at the level of 125 mg/100 g f. w. (**Figure 2g**). The major procyanidins were B-type PC dimers (121 mg/100 g f. w.) and trimers (B-PC tri, 85 mg/100g f. w.). Previously the content of total procyanidins (including epicatechin) in hawthorn fruits, extracted by methanol, was reported to vary in the range of 6-17 mg/g dry mass during fruit ripening (Liu, Kallio, & Yang, 2011). Phenolic acids were the second most abundant group, including 5-*O*-caffeoylquinic acid (5-CQA, 6% of Tot-Ph), 3-*O*-caffeoylquinic acid (5%), 4-*O*-caffeoylquinic acid (4-CQA, 1%), a caffeoylquinic acid isomer (CQA, 2%), and two coumaroylquinic acids (CoQA, 2%). Flavonol glycosides and anthocyanins represented less than 10% of Tot-Ph in hawthorn fruits, primarily as quercetin 3-*O*-glucoside. Cyanidin 3-*O*-galactoside (Cy-Gal, 16 mg/100g f.w.) and peonidin 3-*O*-galactoside (Po-Gal, 2 mg/100g f. w.) were the major anthocyanins.

Flavone *C*-glycosides (luteolin 8-*C*-glucoside, Lu-Glu, and luteolin 8-*C*-glucuronide, Lu-Gluc) and flavanone glycoside (eriodictyol-methyl-hexoside, E-mtHex) were found in trace.

Chokeberry. Anthocyanins in chokeberries were all cyanidin glycosides representing 57% of Tot-Ph (**Figure 2h**). The dominant compounds were 3-*O*-galactoside (222 mg/100g) and 3-*O*-arabinoside (Cy-Ara, 159 mg/100g). This is followed by 3-*O*-caffeoylquinic acid (23% of Tot-Ph) and 5-*O*-caffeoylquinic acid (11%). Flavonol glycosides represented around 10% of Tot-Ph with quercetin 3-*O*-galactoside (Q-Gal) and quercetin 3-*O*-glucoside as the major compounds. Slimestad, Torskangerpoll, Nateland, Johannessen, & Giske, (2005) reported anthocyanins in chokeberries (481 mg/100 g f. w. after extraction by 0.1% hydrochloric acid in methanol) also included mainly cyanidin 3-*O*-galactoside (65% of total anthocyanins) and cyanidin 3-*O*-arabinoside (30%).

Sea buckthorn. Sea buckthorn showed a distinct profile of phenolic compounds compared with other berries, flavonol glycosides being the only phenolic compounds in the berries (**Tables 3**) with similar content and profile in the two Finnish varieties studied (**Figures 2i, 2j)**. Isorhamnetin glycosides corresponded to about 90% of Tot-Ph, the major compounds being 3-*O*-Rutinoside (I-Rut), 3-*O*-sophoroside-7-*O*-rhamnoside (I-SopRha), 3-*O*-glucoside (I-Glu) and 3-*O*-rhamnoside-glucoside-7-*O*-rhamnoside (I-RhaGluRha). Quercetin glycosides accounted for roughly 10% of Tot-Ph in the berries. Compared to our results, the methanol extracts of fruits of sea buckthorn both Finnish and Canadian cultivars contained glycosides of isorhamnetin and quercetin as the major flavonols with a range of 23–250 mg/100 g fresh berries in total (Ma, et al., 2016).

Saskatoon. Saskatoon berries contained mainly phenolic acids and anthocyanins, representing

50% and 40%, respectively, of Tot-Ph (**Figure 2k)**. Caffeoylglyceric acid (CaGA) was isolated and purified by preparative HPLC before NMR analysis (**Table 3**, **Figure 1a**). The content of CaGA was 129 mg/100 g fresh berries, followed by 3-*O*-caffeoylquinic acid (113 mg/100 g f. w.), whereas other phenolic acids were present at clearly lower levels. Cyanidin glycosides were the major anthocyanins (222 mg/100 g f. w.), primarily as 3-*O*-galactoside (Cy-Gal), 3-*O*-glucoside, 3-*O*-arabinoside and 3-*O*-xyloside (Cy-Xyl). Flavonol glycosides (56 mg/100 g f. w.) represented 10% of Tot-Ph, quercetin 3-*O*-galactoside being the most abundant. The total anthocyanin content in the extracts (1% formic acid in 70% acetone) of Finnish saskatoon berries have earlier been reported to vary between 259 and 518 mg/100 g f. w. (Lavola, Karjalainen, & Julkunen-Tiitto, 2012). Cyanidin-based anthocyanins (mostly 3-*O*-galactoside) accounted for 63% of the total phenols but hydroxycinnamic acids were present in those cultivars at a relatively low proportion (Lavola, Karjalainen, & Julkunen-Tiitto, 2012).

Crowberry. As shown in **Figure 2l**, anthocyanins, mainly as anthocyanidin galactosides, were the most abundant phenolic compounds found in crowberry (350 mg/100 g f. w., 80% of Tot-Ph), including malvidin 3-*O*-galactoside (Ma-Gal, 109 mg/100 g), delphinidin 3-*O*-galactoside (De-Gal, 68 mg/100 g), cyanidin 3-*O*-galactoside (66 mg/100 g), petunidin 3-*O*-galactoside (Pt-Gal, 30 mg/100 g) and peonidin 3-*O*-galactoside (23 mg/100 g). Flavonol glycosides added up to 13% of Tot-Ph, and glycosides of isorhamnetin, laricitrin, and syringetin were present as minor compounds. Phenolic acids represented 6% of Tot-Ph.

Rowanberry. Dominated by isomers of caffeoylquinic acids (over 80% of Tot-Phe), the phenolic profile of rowanberry (*Sorbus aucuparia*) clearly differed from other berry samples (**Figure 2m**). 3-*O*-Caffeoylquinic acid and 5-*O*-caffeoylquinic acid were the major isomers,

349 although an unknown isomer of caffeoylquinic acid and a dicaffeoylquinic acid (diCQA)
350 were also detected. Flavonols in the fruits of rowanberry were mostly quercetin glycosides, of
351 which quercetin 3-*O*-(6"-malonyl)-glucoside was close to 50%. (-)-Epicatechin and B-type
352 PC dimers were minor components. Cyanidin 3-*O*-galactoside was the only anthocyanin
353 found in the Finnish cultivar.
354
355 *Cranberry*. In cranberry press cake from juice processing, anthocyanins and flavonol
356 glycosides together represented close to 80% of Tot-Ph (**Figure 2n**). The flavonol glycosides
357 were mainly those of quercetin (31% of Tot-Ph) and myricetin (10% of Tot-Ph). Interestingly,
358 myricetin was also present as aglycone (M agly) at relatively high concentration, probably
359 due to hydrolysis of some glycosides. Anthocyanins in the cranberry press cake were
360 glycosides of cyanidin and peonidin, mainly as 3-*O*-galactoside, 3-*O*-glucoside, and 3-*O*-
361 arabinoside. Only two phenolic acid derivatives were present as 3-*O*-caffeoylquinic acid and
362 caffeic acid (CaA). 1-*O*-benzoyl-*β*-glucose, characterized in the cranberry extract (**Table 2**,
363 **Figure 1b**), represented 7% of Tot-Ph in the press cake (12 mg/100 g).
364
365 3.2 Phenolic compounds in leaves and saskatoon branches analyzed by HPLC-DAD
366 *Lingonberry leaves*. Flavan-3-ols and PC dimers and trimers added up to almost 35% of Tot-
367 Ph in lingonberry leaf (**Figure 3a**). The concentration of (+)-catechin (935 mg/100 g f. w.)
368 significantly exceeded that of (-)-epicatechin (243 mg/100 g). Besides B-type PC dimers (213
369 mg/100 g f. w.), lingonberry leaf also had high levels of A-type procyanidin dimers (A-PC di,
370 397 mg/100 g) and A-type PC trimers (241 mg/100 g). Quercetin glycosides, represented
371 close to 40% of Tot-Ph in lingonberry leaf, mostly as 3-*O*-arabinofuranoside (Q-Araf, 218
372 mg/100 g), 3-*O*-rhamnoside (Q-Rha, 166 mg/100 g), 3-*O*-rutinoside (149 mg/100 g), 3-*O*-

galactoside (148 mg/100 g) and 3-*O*-4"-(3-hydroxy-3-methylglutaroyl)-rhamnoside (Q-hmgRha, 145 mg/100 g). Two derivatives of caffeic acid, caffeoyl-hexose-hydrophenol (Ca-Hex-H) and 3-*O*-caffeoylquinic acid, accounted for 6% of Tot-Ph.

Bilberry leaves. Caffeoylquinic acids represented 80% of Tot-Ph in bilberry leaf, of which 3-*O*-caffeoylquinic acid was the major isomer (1283 mg/100 g f. w., 77% of Tot-Ph) (**Figure 3b**). Liu, Lindstedt, Markkinen, Sinkkonen, Suomela, & Yang (2014) analyzed bilberry leaves during the whole growing season and confirmed the content of this main phenolic compound in 70% aqueous acetone extracts varied dramatically from 2 to 66 mg/g dry mass. A coumaroylquinic acid was also found (33 mg/100 g, f. w.). As the only monomer of flavan-3-ols, (-)-epicatechin was found in bilberry leaf (43 mg/100 g). The procyanidins quantified were mostly B-type PC dimers and trimers. Flavonol glycosides were primarily quercetin 3-*O*-glucuronide (Q-Gluc, 104 mg/100 g f. w.) and kaempferol 3-*O*-glucuronide (K-Gluc, 42 mg/100 g).

Currant leaves. The levels of Tot-Ph in the leaves were similar among different currant cultivars studied. Flavonol glycosides, primiarily derivatives of quercetin and kaempferol accounted for 70-90% of Tot-Ph in these cultivars of *Ribes* spp. **(Figure 3c, 3e and 3f)**. Malonylated flavonol glycosides represented a major fraction of the flavonol glycosides in the leaves of red, green and black currants (**Supplemental Figure 2)**, however being absent in the white currant cultivar. Quercetin 3-*O*-(6"-malonyl)-glucoside was most abundant (251 mg/100 g f. w.) in red currant leaves, followed by green (209 mg/100 g) and black (169 mg/100 g) currant leaves. Kaempferol 3-*O*-(6"-malonyl)-glucoside (K-maGlu) was another major compound of this group (70-100 mg/100 g f. w.) representing 12-18% of Tot-Ph in the leaves. Black currant leaf also contained kaempferol 3-*O*-(6"-malonyl)-galactoside. In white

currant leaf (**Figure 3d**), the major compounds were quercetin 3-*O*-rutinoside, quercetin pentoside-deoxyhexoside-hexoside (Q-PentDeoxHex), kaempferol 3-*O*-rutinoside (K-Rut), quercetin 3-*O*-rhamnoside-rhamnoside-glucoside (Q-RhaRhaGlu), and kaempferol-deoxyhexoside-deoxyhexoside-hexoside (K-DeoxDeoxHex). Apigenin 8-*C*-glucoside was found only in white currant leaf (A-Glu). The total content of the derivatives of phenolic acids varied among the currant cultivars (20-80 mg/100 g f. w., 4-13% of Tot-Ph). 5-*O*-Caffeoylquinic acid (red and black currants) and 3-*O*-caffeoylquinic acid (white and green currants) were the major compounds (**Figure 3d, 3e and 3f**). Even though there are fewer reports on profile of phenolic acids in the leaves of these two species, Mikulic-Petkovsek and coworkers have reported that the content of 5-*O*-caffeoylquinic acid is much more abundant than other hydroxycinnamic acids, which is in agreement with our results. (Mikulic-Petkovseka, et al., 2013)

Hawthorn leaves. Flavonols accounted for more than 50% of Tot-Ph in hawthorn leaves (**Figure 3g**). Extracted by methanol, the contents of total flavonol glycosides in previous research varied in the range of 7–21 mg/g dry mass in hawthorn leaves during autumn, and the total *C*-glycosyl flavone contents varied from 2 to 5 mg/g dry mass (Liu, Kallio, & Yang, 2011). In this study, quercetin 3-*O*-galactoside (184 mg/100 g f. w.) was the primary flavonol glycoside, followed by quercetin 3-*O*-arabinofuranoside (116 mg/100 g). High content of flavone *C*-glycosides was a special feature of the phenolic profile of hawthorn leaf, major compounds being luteolin 8-*C*-glucoside (Lu-Glu, 68 mg/100 g), luteolin 8-*C*-glucuronide (Lu-Gluc, 40 mg/100 g), apigenin 8-*C*-glucoside (30 mg/100 g) and apigenin-methoxyhexoside (A-meHex, 24 mg/100 g). (-)-Epicatechin was the main flavan-3-ol (193 mg/100 g); B-type dimers (113 mg/100 g f. w.) and trimers (123 mg/100 g) were the primary procyanidins quantified in hawthorn leaf. 3-*O*-Caffeoylquinic acid was the only phenolic acid,

corresponding to 12% of Tot-Ph.

Chokeberry leaves, saskatoon leaves and saskatoon branches. The phenolic profiles of chokeberry leaf (**Figure 3h**) and saskatoon leaf (**Figure 3i**) were quite similar, due to dominance of flavonol glycosides and isomers of caffeoylquinic acids, although the presence of individual compounds varied in each group. Both chokeberry and saskatoon are originally North-American native shrubs of Rosaceae family related to each other. Saskatoon leaves have been reported to contain mainly hydroxycinnamic acids (36% of Tot-Ph) as well as quercetin- and kaempferol-derived glycosides (41% of Tot-Ph) (Lavola, Karjalainen, & Julkunen-Tiitto, 2012). Chokeberry leaves differed from the leaves of saskatoon by the strong presence of HP-Hex and practically absence of flavan-3-ols and procyanidins. Furthermore, chokeberry leaves had clearly lower total content of phenolic compounds compared with saskatoon leaves (570 vs. 1500 mg/100 g f. w.). Saskatoon branches (**Figure 3j**) contained the same groups of phenolic compounds as those found in the leaf. However, significantly higher proportions of flavan-3-ols and lower levels of flavonol glycosides and caffeoylquinic acids were found in the branches than in the leaves. This was clearly shown in the total content of phenolic compounds in the branches (500 mg/100 g f. w.), which was one-third of the level found in the leaves (1500 mg/100 g).

Sea buckthorn leaves. The leaves of sea buckthorn showed different phenolic profiles from those of the corresponding berries with the dominance of ellagitannins (above 90% of Tot-Ph). (+)-Catechin and flavonol glycosides together represented the rest of phenolics in sea buckthorn leaves (**Figure 3k and 3l**). Compared with the leaves of the other berry plants, sea buckthorn leaves had a relatively simple profile.

Raspberry leaves. An unknown ellagitannin was found in raspberry leaves at as high content as 1493 mg/100 g f. w. accounting for close to 70% of Tot-Ph (**Figure 3m**). The rest was glycosides of quercetin and kaempferol representing 20% and 10% of Tot-Ph, respectively. As reported previously in blackberries (Wald, Galensa, Herrmann, Grotjahn, & Wray, 1986), quercetin 3-*O*-[6''-(3-hydroxy-3-methylglutaroyl)-*β*-galactoside] (Q-hmgGal) was isolated and determined in raspberry leaves, using preparative HPLC and NMR (**Table 3**, **Figure 1c**); the content of which was up to 72 mg/100 g fresh leaves.

Nettle leaves. The Tot-Ph was lower in nettle leaves than in the leaves of the berry plants. Phenolic acids were the major phenolic compounds (80% of total) in nettle (**Figure 3n & 3o**). The dominant compound was caffeoylmalic acid (CaMA) at a concentration of 97 mg/100 g f. w. in the leaves collected in July and 18 mg/100 g in those collected in October, 2013. The corresponding levels for 3-*O*-caffeoylquinic acid were 41 mg/100 g (July) and 4 mg/100 g (October), respectively. Flavonol glycosides added up to 15-20% of Tot-Ph. Quercetin 3-*O*-rutinoside and 3-*O*-glucoside were the only quercetin derivatives, whereas isorhamnetin 3-*O*-rutinoisde (I-Rut) and kaempferol 3-*O*-rutinoside were minor components. The content of flavonol glycosides was lower in the leaves collected in October compared with the levels in those collected in July.

3.3 NMR profiling of berries and leaves

Twenty-four raw extracts of our samples were analyzed by full-scan NMR, in order to provide an overall profile of the metabolites presented in the extracts (**Supplemental Figure 1**). In overall, aromatic area (all compounds with benzene ring) was richer in signals in berries than in leaves. Caffeic and coumaric acid derivatives showed typically proton signals

from the –HC=CH– double bond (doublets with large coupling constant close to 16 Hz in more common trans isomer) at 6.3-6.6 and 7.5-7.7 ppm. These signals were detected in several berry samples, but not commonly in leaves. Signals at 6.9-7.1 ppm were typical for proton C6 and C8 of flavonoids and proanthocyanidins, which were visible in many berry samples.

In addition to general aspects, some samples showed their own unique features. The signal of prunasin was found in NMR spectra of chokeberry leaves, as well as leaves and branches of saskatoon. Two unknown fractions isolated from saskatoon leaves were confirmed as two prunasin isomers (**Figure 1d**). This compound was quantified by the methods developed for *Prunus serotina* extracts using ^{1}H NMR (Santos Pimenta, Schilthuizen, Robert, & Choi, 2013). The highest prunasin content, 730 mg/100 g f. w., was found in saskatoon branches. Saskatoon leaves and chokeberry leaves contained prunasin at levels of 210 and 370 mg/100 g f. w., respectively. Prunasin is a cyanogenic glycoside, which could release hydrogen cyanide, a toxic compound, through the reaction glucosidases in the plant material or in the digestive track of the consumer. The cyanogenic potential of saskatoon leaves, saskatoon branches and chokeberry leaves should be taken into account when estimating the safety of these materials as raw materials of food and food additives.

The dominant aromatic signals of crude extracts of white and red currant leaves, shown in **Supplemental Figure 1**, came from an aromatic tyramine. ^{1}H NMR spectra of the extracts showed two-fold doublets δ 7.13 (H2 and H6) and 6.81 (H3 and H5) with couplings of 8.4 Hz, indicating a para-substituted aryl ring. The phenylethyl backbone structure was characterized by an HMBC correlation from H2 and H6 to carbon δ 35.2 (C7) and a COSY correlation from the corresponding proton of C7 (H7, δ 2.88) to adjacent methylene protons δ 3.14.

(**Figure 1e**) The ^{1}H and ^{13}C NMR spectra were in accordance with the chemical shifts of the external reference compound. Since tyramine was not identified in the extracts of green currant and black currant leaves (*Ribes nigrum* L.), the signals of tyramine in the ^{1}H NMR spectrum could serve as a chemotaxonomic marker, differentiating *R. rubrum* from *R. nigrum*. However, the content of tyramine was unmeasurable in this study, due to no typical peaks and fragments shown in HPLC chromatograph and MS spectra of corresponding extracts, respectively.

β-Arbutin identified in the extract of lingonberry leaves is in accordance with literature (Liu, Lindstedt, Markkinen, Sinkkonen, Suomela, & Yang, 2014). The para-substituted aryl ring of β-arbutin was proved by two-fold doublet (8.9 Hz) signals δ 7.00 (H2 and H6) and 6.77 (H3 and H5). The HMBC correlations from H3, H5 and H1' (anomeric proton of glucose, δ 4.82) showed a correlation to carbon δ 154.0 (C1). As shown in **Figure 3a**, the concentration of β-arbutin in lingonberry leaf was up to 2711 mg/100 g fresh leaves (44% of Tot-Ph).

Furthermore, ethyl β-glucoside (anomeric proton at 4.36 ppm) was only found in sea buckthorn berries at detectable concentrations, but the total concentration of glucose was still lower than that in other berries in general. Citric acid (two doublets at 2.8 and 2.9 ppm) was clearly visible in black currant press cake.

4. Conclusion

This research is the first one providing systematic and thorough information on the phenolic compounds in extracts obtained with an extraction protocol using a food grade solvent, which can be up-scaled and applied in food industry. Over 160 phenolic compounds were analyzed using NMR, UPLC-DAD-ESI-MS, and HPLC-DAD mainly covering flavan-3-ols,

proanthocyanidins, ellagitannins, anthocyanins, phenolic acid derivatives, flavonol glycosides, flavone glycosides, and flavanone glycosides. Overall, leaves were richer sources of phenolics than berries. The leaves within higher total content of phenolics were sea buckthorn leaves (mainly as ellagitannins), lingonberry leaf (flavan-3-ols, proanthocyanidins and flavonol glycosides), raspberry leaf (ellagitannins), and bilberry leaf (phenolic acid derivatives). Asides from anthocyanins being dominant in dark-skin berries, phenolic acid derivatives represented high level in saskatoon berry, chokeberry and rowan berry. Proanthocyanidins were abundant in hawthorn fruits, which was very exceptional among the berries included in the current study. The presence of other aromatic compounds shall be considered when evaluating the safety aspects of the raw materials for potential use as food ingredients.

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Appendix A. Abbreviations used

All abbreviations used in this study are listed as below:

high performance liquid chromatography (**HPLC**), mass spectrometry (**MS**), nuclear magnetic resonance spectroscopy (**NMR**), 3-(trimethylsilyl) propionic-2,2,3,3-d_4 acid sodium salt (**TSP**), deuterium oxide (**D_2O**), methanol-d_4 (**CD_3OD**), total correlated spectroscopy (**TOCSY**), double-quantum filtered correlation spectroscopy (**DQF-COSY**), heteronuclear single-quantum correlation spectroscopy (**HSQC**), heteronuclear multiple-bond correlation spectroscopy (**HMBC**), ultra-performance liquid chromatography (**UPLC**), photodiode array detector (**DAD**), ultraviolet–visible spectroscopy (**UV-VIS**), total content of phenolics (**Tot-Ph**), fresh weight, (**f. w.**), (+)-catechin (**(+)-Cat**), (-)-epicatechin (**(-)-Epic**), A/B-type procyanidin dimers/trimers (**A/B-PC di/tri**), bis(hexahydroxydiphenoyl)-hexoside (**bisHHDP-Hex**), ellagitannin (**Et**), galloyl-bis(hexahydroxydiphenoyl)-hexoside (**G-bisHHDP-Hex**), 4-(2-hydroxyethyl)phenol-hexoside (**HP-Hex**) vanillic acid-hexoside (**VA-Hex**), coumaric acid-hexoside (**CoA-Hex**), caffeic acid-hexoside (**CaA-Hex**), coumaroylquinic acid (**CoQA**), ferulic acid-hexoside (**FA-Hex**), cafferol-hexose-hydrophenol (**Ca-Hex-H**), caffeic acid (**CaA**), *p*-coumaric acid (***p*-CoA**), 5/3/4-*O*-caffeoylquinic acid (**5/3/4-CQA**), dicaffeoylquinic acid (**diCQA**), caffeoylmalic acid (**CaMA**), caffeoylglyceric acid (**CaGA**), 1-*O*-benzoyl-β-glucose (**BA-Glu**), quercetin (**Q**), myricetin (**M**), isorhamnetin (**I**), kaempferol (**K**), laricitrin (**La**), syringetin (**S**), apigenin (**A**), luteolin (**Lu**), eriodictyol (**E**), cyanidin (**Cy**), delphinidin (**De**), petunidin (**Pt**), peonidin (**Po**),malvidin (**Ma**), rutinoside (**Rut**), galactoside (**Gal**), glucoside (**Glu**), hexoside (**Hex**), rhamnoside (**Rha**), deoxyhexoside (**Deox**), xyloside (**Xyl**), arabinoside (**Ara**), arabinofuranoside (**Araf**), pentoside (**Pent**), glucuronide (**Gluc**), coumaroyl-glucoside (**coGlu**), hydroxy-methylglutaroyl-galactoside (**hmgGal**), hydroxy-methylglutaroyl-galactoside (**hmgRha**), benzoyl-galactoside/glucoside (**beGal**/**Glu**), malonyl-galactoside/ glucoside (**maGal**/**Glu**), feruloyl-glucoside (**feGlu**), acetyl-glucoside (**acGlu**), methoxyhexoside (**meHex**), methyl-hexoside (**mtHex**), dihexoside (**diHex**), neohesperidoside (**Neo**), and *β*-arbutin (**Arb**).

571

572 **Appendix B. Supporting Information description**

573 The supporting information is provided: (1) NMR full spectra of extracts of different
574 materials studied (**Supplemental Figure 1**). (2) HPLC chromatographs of extracts of some
575 materials studied (**Supplemental Figure 2**).

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750 **Figure captions**

751 **Figure 1**: Structures and NMR information of some compounds isolated and purified from
752 samples

753 **Figure 2**: Concentration (mg/100g, fresh weight) and percentage of phenolic compounds in
754 berries

755 **Figure 3**: Concentrations (mg/100g, fresh weight) and percentage of phenolic compounds in
756 leaves and saskatoon branch

Table 1

Table 1 Names, abbreviations and sources of plant materials studied

sample name	Abbreviation	Latin name	Collection site / source
Lingonberry	LB	*Vaccinium vitis-idaea*	Laarikallio Rauma, Paattinen, Turku, Finland
Lingonberry leaf	LBL		
Bilberry	BB	*Vaccinium myrtillus*	
Bilberry leaf	BBL		
Red currant	RC	*Ribes rubrum 'Red Dutch'*	
Red currant leaf	RCL		
White currant	WC	*Ribes rubrum 'White Dutch'*	Agrifood Research Finland, Piikkiö, Finland
White currant leaf	WCL		
Green currant	GC	*Ribes nigrum 'Vertti'*	
Green currant leaf	GCL		
Black currant press cake	BCPC	*Ribes nigrum 'Mortti'*	Saarioinen Oy, Finland
Black currant leaf	BCL		Agrifood Research Finland, Piikkiö, Finland
Hawthorn	HT	*Crataegus grayana*	Campus of University of Turku, Turku, Finland
Hawthorn leaf	HTL		
Chokeberry	CKB	*Aronia melonocarpa*	Agrifood Research Finland, Piikkiö, Finland
Chokeberry leaf	CKL		
Sea buckthorn_Terhi	SB_Terhi	*Hippophaë rhamnoides ssp. rhamnoides 'Terhi'*	Sammalmäki, Turku, Finland
Sea buckthorn leaf_Terhi	SBL_Terhi		
Sea buckthorn_Tytti	SB_Tytti	*Hippophaë rhamnoides ssp. rhamnoides 'Tytti'*	
Sea buckthorn leaf_Tytti	SBL_Tytti		
Saskatoon berry	SK	*Amelanchier alnifolia*	Linnan Marjatila Oy, Lohja, Finland
Saskatoon leaf	SKL		
Saskatoon branch	SKB		
Nettle_Oct.	N_Oct	*Urtica dioica*	Perniö, Finland
Nettle_Jul.	N_Jul		
Crowberry	CB	*Empetrum nigrum*	Marjajaloste Meritalo Oy, Ylönkylä, Finland
Rowan berry	RB	*Sorbus aucuparia*	Agrifood Research Finland, Piikkiö, Finland
Cranberry press cake	CBPC	*Vaccinium oxycoccos*	Marjajaloste Meritalo Oy, Ylönkylä, Finland
Raspberry leaf	RBL	*Rubus idaeus*	Agrifood Research Finland, Piikkiö, Finland

Table 2

Table 2 Abbreviations of phenolic compounds in materials studied

Full name	Abbreviation	Full name	Abbreviation	Full name	Abbreviation
Flavan-3-ols					
(+)-catechin	(+)-Cat	(-)-epicatechin	(-)-Epic		
Proanthocyanidins					
A/B-type procyanidin dimers	A/B-PC di	A/B-type procyanidin trimers	A/B-PC tri		
Ellagitannins					
bis(hexahydroxydiphenoyl)-hexoside	bisHHDP-Hex	unknown ellagitannin	Et unkown	galloyl-bis(hexahydroxydiphenoyl)-hexoside	G-bisHHDP-Hex
Phenolic acid derivatives					
4-(2-hydroxyethyl)phenol-hexoside	HP-Hex	vanillic acid-hexoside	VA-Hex	coumaric acid-hexoside	CoA-Hex
caffeic acid-hexoside	CaA-Hex	coumaroylquinic acid	CoQA	ferulic acid-hexoside	FA-Hex
cafferol-hexose-hydrophenol	Ca-Hex-H	caffeic acid	CaA	*p*-coumaric acid	*p*-CoA
5-*O*-caffeoylquinic acid	5-CQA	3-*O*-caffeoylquinic acid	3-CQA	4-*O*-caffeoylquinic acid	4-CQA
caffeoylquinic acid isomer	CQA	dicaffeoylquinic acid	diCQA	caffeoylmalic acid	CaMA
caffeoylglyceric acid	CaGA	1-*O*-benzoyl-*β*-glucose	BA-Glu		
aglycones of Other Flavanoids					
quercetin	Q	myricetin	M	isorhamnetin	I
kaempferol	K	laricitrin	La	syringetin	S
apigenin	A	luteolin	Lu	eriodictyol	E
cyanidin	Cy	delphinidin	De	petunidin	Pt
peonidin	Po	malvidin	Ma		
saccharides of Other Flavanoids					
rutinoside	Rut	galactoside	Gal	glucoside	Glu
hexoside	Hex	rhamnoside	Rha	deoxyhexoside	Deox
xyloside	Xyl	arabinoside	Ara	arabinofuranoside	Araf
pentoside	Pent	glucuronide	Gluc	coumaroyl-glucoside	coGlu
hydroxy-methylglutaroyl-galactoside	hmgGal	hydroxy-methylglutaroyl-galactoside	hmgRha	benzoyl-galactoside	beGal
benzoyl-glucoside	beGlu	malonyl-galactoside	maGal	malonyl-glucoside	maGlu
feruloyl-glucoside	feGlu	acetyl-glucoside	acGlu	methoxyhexoside	meHex
methyl-hexoside	mtHex	dihexoside	diHex	neohesperidoside	Neo
Other phenolic compounds					
β-Arbutin	Arb				

Table 3

Table 3. Identification of phenolic compounds in different materials by UPLC-DAD-MS

Tentative identification	Abbreviation	Occurrence in samples[a]	UV λ_{max} (nm)	$[M+H]^+$/ $[M-H]^-$ (m/z)	$[A+H]^+$/ $[A-H]^-$ and other ions (m/z)	Identification by[b]
Flavan-3-ols						
(+)-catechin	(+)-Cat	LB,RC,WC,GC,LBL,WCL, GCL,BCL,SBL,SKB	280	291/289		standard
(-)-epicatechin	(-)-Epic	LB,RB,HT,GC,LBL,BBL, SKL,HTL,SKB	280	291/289		standard
Proanthocyanidins						
B-type procyanidin dimers	B-PC di	LB,RB,HT,LBL,BBL,SKL, HTL,SKB	280	579/577	291/289	literature [1]
B-type procyanidin trimers	B-PC tri	HT,BBL,SKL,HTL,SKB	280	867/865	579,291/577,289	literature [1]
A-type procyanidin dimers	A-PC di	LBL	279	577/575	291/289	literature [1]
A-type procyanidin trimers	A-PC tri	LBL	280	865/863	575,291/573,289	literature [1]
Ellagitannins						
bis(hexahydroxydiphenoyl)-hexoside 1	bisHHDP-Hex 1	SBL	280	785/783	483,303/481,301	literature [2,3]
bis(hexahydroxydiphenoyl)-hexoside 2	bisHHDP-Hex 2	SBL	280	785/783	483,303/481,301	literature [2,3]
galloyl-bis(hexahydroxydiphenoyl)-hexoside 1	G-bisHHDP-Hex 1	SBL	280	937/935	635,303/633,301	literature [2,3]
galloyl-bis(hexahydroxydiphenoyl)-hexoside 2	G-bisHHDP-Hex 2	SBL	280	937/935	635,303/633,301	literature [2,3]
galloyl-bis(hexahydroxydiphenoyl)-hexoside 3	G-bisHHDP-Hex 3	SBL	280	937/935	635,303/633,301	literature [2,3]
galloyl-bis(hexahydroxydiphenoyl)-hexoside 4	G-bisHHDP-Hex 4	SBL	280	937/935	635,303/633,301	literature [2,3]
unknown ellagitannin 1	Et unkown 1	RBL	256	936/934	303/633,301	MS
unknown ellagitannin 2	Et unkown 2	SBL	280	955/953	635,303/633,301	MS
Phenolic acid derivatives						
vanillic acid-hexoside	VA-Hex	RC,WC,GC,WCL	268,295(sh)	331/329	169/167	literature [5]
coumaric acid-hexoside 1	CoA-Hex 1	RC,WC,GC	280(sh),320	327/325	165/163	literature [5]
coumaric acid-hexoside 2	CoA-Hex 2	RC,WC,GC	280(sh),320	327/325	165/163	literature [5]
coumaric acid-hexoside 3	CoA-Hex 3	RC,WC,GC	280(sh),320	327/325	165/163	literature [5]
coumaric acid-hexoside 4	CoA-Hex 4	WC,GC	280(sh),320	327/325	165/163	literature [5]
caffeic acid-hexoside 1	CaA-Hex 1	RC,WC,GC,BCL	295(sh),329	343/341	181/179	literature [5]
caffeic acid-hexoside 2	CaA-Hex 2	RC,WC,GC,BCL	295(sh),329	343/341	181/179	literature [5]
coumaroylquinic acid 1	CoQA 1	CB,HT,BBL,SKL	290(sh),310	339/337	-/163,191	literature [5]
coumaroylquinic acid 2	CoQA 2	N_Jul,HT,BBL,SKL	290(sh),313	339/337	-/163,191	literature [5]
ferulic acid-hexoside 1	FA-Hex 1	WC,GC	284(sh),322	357/355	195/193	literature [5]
ferulic acid-hexoside 2	FA-Hex 2	LB	284(sh),322	357/355	195/193	literature [5]
ferulic acid-hexoside 3	FA-Hex 3	LB	284(sh),322	357/355	195/193	literature [5]
5-*O*-caffeoylquinic acid	5-CQA	CB,RB,CKB,SK,HT,CKL, SKL,RCL,BCL,SKB	295(sh),322	355/353	163/191	standard

3-*O*-caffeoylquinic acid	3-CQA	LB,RB,N-Oct,N-Jul,CKB, SK,CBPC,HT,LBL,BBL, CKL,SKL,HTL,WCL,GCL, BCL,SKB	290(sh),326	355/353	163/191	standard
4-*O*-caffeoylquinic acid	4-CQA	HT,LBL	285(sh),326	355/353	163/191	standard
caffeoylquinic acid isomer	CQA	RB,HT,BBL,SKL,SKB	290(sh),318	355/353	163/191	literature [6]
dicaffeoylquinic acid	diCQA	RB,CKB,SK,CKL,SKL	295(sh),328	517/515	355,163/353,191	literature [6,7]
cafferol-hexose-hydrophenol	Ca-Hex-H	LBL	290(sh),329	435/433	325,163/323,161	literature [8]
caffeoylmalic acid	CaMA	N-Oct,N-Jul,SK,SKL	295(sh),329	297/295	163/179	literature [9]
caffeoylglyceric acid	CaGA	SK	295(sh),329	269/267	163/179	NMR and literature [9]
caffeic acid	CaA	CBPC	288(sh),325	181/179		literature [4,5]
p-coumaric acid	p-CoA	BCPC	290(sh),310	165/163		literature [4,5]
1-*O*-benzoyl-*β*-glucose	BA-Glu	LB,CB	234, 275	285/283	307/567	NMR and literature [10]
Flavonol glycosides						
quercetin 3-*O*-sophoroside-7-*O*-rhamnoside	Q-SopRha	SB	256,268(sh),355	773/771	611,449,303/-	literature [11]
quercetin-dihexoside 1	Q-diHex 1	RB,CKB,CKL	255,268(sh),352	627/625	465,303/301	MS
quercetin-dihexoside 2	Q-diHex 2	RB,CKB,CKL	255,268(sh),352	627/625	465,303/301	MS
quercetin 3-*O*-rhamnoside-rhamnoside-glucoside	Q-RhaRhaGlu	SB,WC,WCL,CKL	256,267(sh),355	757/755	611,465,303/-	literature [11]
quercetin 3-*O*-rhamnosylglucoside-7-*O*-rhamnoside	Q-RhaGluRha	SB	256,267(sh),355	757/755	611,449,303/609	literature [12]
quercetin-deoxyhexoside-hexoside-deoxyhexoside	Q-DeoxHexDeox	CKL	255,267(sh),355	757/755	611,465,303/-	MS
quercetin 3-*O*-glucoside-7-*O*-rhamnoside	Q-GluRha	SBL	255,268(sh),350	611/609	449,303/301	literature [11]
quercetin-pentoside	Q-Pent	SBL	254,268(sh),360	435/433	303/301	MS
quercetin 3-*O*-(6-*O*-feruloylglucoside)-glucoside-7-*O*-rhamnoside	Q-feGluGluRha	SBL	254,267(sh),340	949/947	303/301	literature [11]
quercetin-pentoside-deoxyhexoside-hexoside	Q-PentDeoxHex	WC,WCL	255,266(sh),355	743/741	611,465,303/625,463	MS
quercetin-pentoside-hexoside	Q-PentHex	WCL	256,268(sh),356	597/595	465,303/301	MS
quercetin-deoxyhexoside-hexoside 1	Q-DeoxHex 1	WCL	256,268(sh)356	611/609	465,303/301	MS
quercetin-arabinoglucoside	Q-AraGlu	SK,CKB,WC,CKL,SKL, HTL,SKB	254,268(sh),352	597/595	465,303/301	literature [13]
quercetin-pentoside-glucuronide	Q-PentGluc	RBL	256,268(sh),354	611/609	479,303/301	MS
quercetin-deoxyhexoside-hexoside 2	Q-DeoxHex 2	SK,CKB,CKL,SKL,HTL, SKB	256,267(sh),355	611/609	303/301	MS
quercetin 3-*O*-rutinoside	Q-Rut	LB,CB,RB,N-Oct,N-Jul, BCPC,SK,CKB,SB,HT,RC, WC,GC,LBL,RCL,GCL, WCL,BCL,CKL,SBL,SKB	256,265(sh),354	611/609	465,303/301	standard
quercetin 3-*O*-galactoside	Q-Gal	LB,CB,RB,CBPC,BB,SK, CKB,LBL,BBL,BCL,CKL, SKL,RBL,HTL,SKB	254,266(sh),354	465/463	303/301	standard
quercetin 3-*O*-glucoside	Q-Glu	LB,CB,RB,N,CBPC,BCPC, BB,SK,CKB,SB,HT,RC,	254,268(sh),354	465/463	303/301	standard

quercetin 3-*O*-glucuronide	Q-Gluc	WC,GC,LBL,RCL,GCL, WCL, BCL,CKL,SKL,HTL,SKB BB,BBL,RBL	256,266(sh),355	479/477	303/301	standard
quercetin 3-*O*-[6’’-(3-hydroxy-3-methylglutaroyl)-*β*-galactoside]	Q-hmgGal	RBL	257,269(sh),356	609/607	449,303/463,301	NMR and literature [14]
quercetin 3-*O*-xyloside	Q-Xyl	LB,CBPC,SKB,HT,LBL, SKL,HTL,SKB	254,267(sh),353	435/433	303/301	literature [8,15,16]
quercetin 3-*O*-arabinoside	Q-Ara	LB,CB,CBPC,SK,CKB,HT, LBL,BCL,SKL,HTL,SKB	254,267(sh),353	435/433	303/301	literature [8,15,16]
quercetin 3-*O*-arabinofuranoside	Q-Araf	LB,CB,CBPC,SK,LBL, SKL,HTL	254,267(sh),353	435/433	303/301	literature [8,15,16]
quercetin 3-*O*-rhamnoside	Q-Rha	LB,CBPC,LBL	255,265(sh),352	449/447	303/301	standard
quercetin 3-*O*-4"-(3-hydroxy-3-methylglutaroyl)-rhamnoside	Q-hmgRha	LB,LBL	255,265(sh),348	593/591	303/301	literature [8,15,16]
quercetin 3-*O*-(6’’-benzoyl)-galactoside	Q-beGal	LB,CB,CBPC	255,268(sh),355	569/567	303/301	literature [17,18]
quercetin 3-*O*-(6"-malonyl)-galactoside	Q-maGal	RB	256,268(sh),357	551/549	303/505,301	MS
quercetin 3-*O*-(6"-malonyl)-glucoside	Q-maGlu	RB,BCPC,SK,CKB,RC,GC ,RCL,GCL,BCL,SKL,SKB	256,268(sh),356	551/549	303/505,301	standard
quercetin 3-*O*-(6"-acetyl)-glucoside	Q-acGlu	HT,HTL	254,268(sh),351	507/505	303/463,301	literature [19]
quercetin	Q agly	BCPC,SK	274,368	303/301		standard
myricetin 3-*O*- rutinoside	M-Rut	BCPC,GC,GCL	268,356	627/625	481,319/317	literature [19]
myricetin 3-*O*-galactoside	M-Gal	CB,CBPC,BB,RC	265,354	481/479	319/317	standard
myricetin 3-*O*-glucoside	M-Glu	CB,CBPC,BCPC,BB,WC, GC,GCL	265,356	481/479	319/317	standard
myricetin 3-*O*-glucuronide	M-Gluc	BB	267,352	495/493	319/317	literature [19]
myricetin 3-*O*- xyloside	M-Xyl	CBPC	267,356	451/449	319/317	literature [20]
myricetin 3-*O*-arabinoside	M-Ara	CBPC	267,354	451/449	319/317	literature [20]
myricetin 3-*O*-arabinofuranoside	M-Araf	CB,CBPC	267,354	451/449	319/317	literature [19]
myricetin-benzoyl-galactoside	M-beGal	CB	275,371	585/583	319/317	MS
myricetin-benzoyl-glucoside	M-beGlu	CB	271,359	585/583	319/317	MS
myricetin 3-*O*-(6"-malonyl)-glucoside	M-maGlu	BCPC,GC,GCL	269,360	567/565	319/521,317	literature [19]
myricetin	M agly	CBPC,BCPC	266,374	319/317		standard
isorhamnetin 3-*O*-neohesperidoside-7-*O*-glucoside	I-NeoGlu	SB,SBL	256,268(sh),355	787/785	625,463,317/639,465	literature [11,12]
isorhamnetin 3-*O*-sophoroside-7-*O*-rhamnoside	I-SopRha	SB,SBL	256,268(sh),355	787/785	625,463,317/ 465	literature [11]
isorhamnetin-hexoside-deoxyhexoside-hexoside	I-HexDeoxHex	SBL	256,268(sh),355	787/785	625,463,317/-	MS
isorhamnetin 3-*O*-rhamnoside-rhamnoside-glucoside	I-RhaRhaGlu	SB	254,268(sh),354	771/769	625,479,317/-	literature [11]
isorhamnetin 3-*O*-rhamnoside-glucoside-7-*O*-rhamnoside	I-RhaGluRha	SB	254,268(sh),354	771/769	625,463,317/623,477,461	literature [11]
isorhamnetin 3-*O*-glucoside-7-*O*-rhamnoside	I-GluRha	SB,SBL	255,267(sh),355	625/623	449,317/447,315	literature [11,21,22]
isorhamnetin 3-*O*-(6-*O*-feruloylglucoside)-glucoside-7-*O*-rhamnoside	I-feGluRha	SBL	255,269(sh),355	963/961	317/315	literature [11]
isorhamnetin-pentoside-hexoside 1	I-HexPent 1	CKB	273,352	611/609	479,317/315	MS
isorhamnetin-hexoside-pentoside 2	I-HexPent 2	CKL	255,268(sh),352	611/609	449,317/315	MS
isorhamnetin 3-*O*-neohesperidoside	I-Neo	CKB,SB	268,351	625/623	479,317/315	literature [12]

isorhamnetin 3-*O*-rutinoside	I-Rut	CB,N-Oct,N-Jul,BCPC, CKB,SB,GC,CKL,HTL, SBL, SKB	254,265(sh),355	625/623	479,317/315	standard
isorhamnetin 3-*O*-galactoside	I-Gal	SKB	255,267(sh),355	479/477	317/315	literature [19]
isorhamnetin 3-*O*-glucoside	I-Glu	SB,GC,SBL	255,265(sh),354	479/477	317/315	standard
isorhamnetin-pentoside 1	I-Pent 1	HTL	254,267(sh),350	449/447	317/315	MS
isorhamnetin-pentoside 2	I-Pent 2	HTL	254,267(sh),350	449/447	317/315	MS
isorhamnetin 3-*O*-(6"-malonyl)-glucoside	I-maGlu	GC	269,355	565/563	317/447,315	MS
isorhamnetin-trideoxyhexoside+hexoside	I-triDeoxHex	SB	256,269(sh),359	917/915	463,317/769,477,315	MS
unknown isorhamnetin glycoside	I unkown	SBL	255,267(sh),355	791/789	629,482/627,477,315	MS
isorhamnetin	I agly	CBPC	257,373	317/315		MS
kaempferol-deoxyhexoside-deoxyhexoside-hexoside	K-DeoxDeoxHex	WC,WCL	266,348	741/739	595,449,287/-	MS
kaempferol-pentoside-deoxyhexoside-hexoside	K-PentDeoxHex	WCL	266,349	727/725	595,449,287/-	MS
kaempferol-hexoside-pentoside	K-HexPent	WCL,CKL,SKL	266,347	581/579	449,287/285	MS
kaempferol 3-*O*-rutinoside	K-Rut	N-Jul,WC,GC,RCL,WCL, BCL,CKL,SBL,SKB	266,348	595/593	449,287/285	standard
kaempferol-pentoside-glucuronide	K-PentGluc	RBL	266,347	595/593	463,287/285	MS
kaempferol 3-*O*-glucoside	K-Glu	CKB,GC,RCL,GCL,WCL, BCL,CKL,SKL,RBL	265,348	449/447	287/285	standard
kaempferol 3-*O*-glucuronide	K-Gluc	BBL,RBL	266,347	463/461	287/285	standard
kaempferol-pentoside 1	K-Pent 1	BCL,HTL	267,349	419/417	287/285	literature [23]
kaempferol-pentoside 2	K-Pent 2	HTL	267,349	419/417	287/285	MS
kaempferol 3-*O*-(6"-malonyl)-galactoside	K-maGal	BCL	266,349	535/533	287/489,285	literature [23]
kaempferol 3-*O*-(6"-malonyl)-glucoside	K-maGlu	RC,GC,RCL,GCL,BCL	266,349	535/533	287/489,285	literature [23]
kampferol 3-*O*-4"-(3-hydroxy-3-methylglutaroyl)-rhamnoside	K-hmgRha	LBL	265,340	577/575	287/285	literature [8,15,16]
unknown kaempferol glycoside	K unkown	RBL	266,349	593/591	465,441,287/529,489,447,285	MS
kaempferol 3-*O*-neohesperidoside	K-Neo	SBL	267,315	595/593	287/447,285	literature [12,19]
kaempferol-rhamnosylhexoside	K-RhaHex 2	RBL,SBL	267,315	595/593	287/447,285	literature [19]
kaempferol	K agly	CBPC	268,366	287/285		standard
laricitrin 3-*O*-galactoside	La-Gal	CB	266,358	495/493	333/331	literature [20]
laricitrin 3-*O*-glucoside	La-Glu	CB	268,356	495/493	333/331	literature [20]
laricitrin-pentoside	La-Pent	CB	273,354	465/463	333/331	literature [20]
laricitrin 3-*O*-(6"-malonyl)-hexoside	La-maHex	GC	269,355	581/579	333/535,331	MS
syringetin 3-*O*-rutinoside	S-Rut	GC	269,355	655/653	509,347/345	literature [19]
syringetin 3-*O*-galactoside	S-Gal	CB	268,356	509/507	347/345	literature [20]
syringetin 3-*O*-glucoside	S-Glu	CB,BB	268,356	509/507	347/345	standard
syringetin-pentoside	S-Pent	CB	270,352	449/447	347/345	literature [20]
syringetin -malonyl-hexoside	S-maHex	GC	270,356	595/593	347/549,345	MS
Flavone glycosides						
apigenin 8-*C*-glucoside	A-Glu	WCL,HTL	267,338	433/431	271/269	literature [24]
apigenin-methoxyhexoside	A-meHex	HTL	268,347	463/461	301/299,269	MS

luteolin 8-*C*-glucoside	Lu-Glu	HT,HTL	255,268(sh),350	449/447	287/285	literature [24]
luteolin 8-*C*-glucuronide	Lu-Gluc	HT,HTL	255,267(sh),349	463/461	287/285	literature [24]
Flavanone glycosides						
eriodictyol 7-*O*-glucoside	E-Glu	SKB	284,322	451/449	289/287	literature [25]
eriodictyol-methyl-hexoside	E-mtHex	HT	284,330	465/463	289/287	MS
Anthocyanins						
cyanidin 3,5-*O*-diglucoside	Cy-diGlu	RC	281,516	611/609	287/285	literature [26]
cyanidin 3-*O*-glucosylrutinoside	Cy-GluRut	RC	281,518	757/755	287/285	literature [26]
cyanidin 3-*O*-xylosylglucoside	Cy-XylGlu	RC	280,518	581/579	287/285	literature [26]
cyanidin 3-*O*-xylosylrutinoside	Cy-XylRut	RC	281,523	727/725	287/285	literature [26]
cyanidin 3-*O*-rutinoside	Cy-Rut	BCPC,RC	281,524	-/593	-/285	standard
cyanidin 3-*O*-galactoside	Cy-Gal	LB,BB,CKB,SK,RB,CB, CBPC,HT	280,520	-/447	-/285	literature [13]
cyanidin 3-*O*-glucoside	Cy-Glu	LB,BB,CKB,SK,CBPC, BCPC	280,520	-/447	-/285	standard
cyanidin 3-*O*-arabinoside	Cy-Ara	LB,BB,CKB,SK,CB,CBPC	280,520	-/417	-/285	standard
cyanidin 3-*O*-xyloside	Cy-Xyl	CKB,SK	280,520	-/417	-/285	literature [13]
cyanidin-pentoside	Cy-Pent	LB	280,520	-/417	-/285	MS
cyanidin 3-*O*-(6"-coumaroyl)-glucoside	Cy-coGlu	BCPC	283,524	-/593	-/447,285	literature [26,27]
cyanidin 3-*O*-(6"-acetyl)-glucoside	Cy-acGlu	LB	280,520	-/489	-/285	literature [27]
delphinidin 3-*O*-rutinoside	De-Rut	BCPC	274,524	-/609	-/301	literature [27]
delphinidin 3-*O*-galactoside	De-Gal	BB,CB,BCPC	276,522	-/463	-/301	literature [28]
delphinidin 3-*O*-glucoside	De-Glu	BB	278,524	-/463	-/301	standard
delphinidin 3-*O*-arabinoside	De-Ara	BB,CB	277,523	-/433	-/301	literature [28]
delphinidin 3-O-(6"-coumaroyl)-glucoside	De-coGlu	BCPC	282,524	-/609	-/447,301	literature [27]
petunidin 3-*O*-rutinoside	Pt-Rut	BCPC	278,524	-/623	-/477,315	literature [27]
petunidin 3-*O*-galactoside	Pt-Gal	BB,CB	278,522	-/477	-/315	literature [28]
petunidin 3-*O*- glucoside	Pt-Glu	BB	277,519	-/477	-/315	literature [28]
petunidin 3-*O*-arabinoside	Pt-Ara	BB,CB	279,523	-/447	-/315	literature [28]
peonidin 3-*O*-galactoside	Po-Gal	BB,CB,CBPC,HT	281,522	-/461	-/299	literature [28-45]
peonidin 3-*O*-glucoside	Po-Glu	BB,CBPC	280,522	-/461	-/299	literature [28-45]
peonidin 3-*O*-arabinoside	Po-Ara	CB,CBPC	281,522	-/431	-/299	literature [29-45]
malvidin 3-*O*-galactoside	Ma-Gal	BB,CB	281,522	-/491	-/329	literature [28]
malvidin 3-*O*-glucoside	Ma-Glu	BB,CB	281,522	-/491	-/329	standard
malvidin 3-*O*-arabinoside	Ma-Ara	BB,CB	281,522	-/461	-/329	literature [28]
Other phenolic compounds						
4-(2-hydroxyethyl)phenol-hexoside	HP-Hex	RC,WC,GC,CKL,WCL	263	301/299	139/137	literature [4]
β-arbutin	Arb	LBL	282	-/271	-/543	NMR and literature [30]

a. Abbreviations and the full names of samples are listed as below:

lingonberry (LB), lingonberry leaf (LBL); bilberry (BB), bilberry leaf (BBL); red currant (RC), red currant leaf (RCL); white currant (WC), white currant leaf (WCL); green currant (GC), green currant leaf (GCL); black currant press cake (BCPC), black currant leaf (BCL); hawthorn (HT), hawthorn leaf (HTL); chokeberry (CKB), chokeberry leaf (CKL); saskatoon berry (SK), saskatoon branch (SKB), saskatoon leaf (SKL); two cultivars of sea buckthorn berries (SB), two cultivars of sea buckthorn leaves (SBL); cranberry press cake (CBPC); raspberry leaf (RBL); nettle-October 2013 (N-Oct), nettle-July 2013 (N-Jul); crowberry (CB); rowanberry (RB).

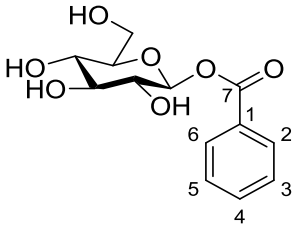
b. Reference literatures are listed as below:

1. Kallio, Yang, Liu, & Yang, 2014; 2. Buendía, et al., 2010; 3. Santos, Freire, Domingues, Silvestre, & Pascoal Neto, 2011; 4. Chiou, Karathanos, Mylona, Salta, Preventi, & Andrikopoulos, 2007; 5. Fang, Yu, & Prior, 2002; 6. Lee, et al., 2014; 7. Lin, & Harnly, 2007; 8. Hokkanen, Mattila, Jaakola, Pirttila, & Ari Tolonen, 2009; 9. Hahn, & Nahrstedt, 1993; 10. Heimhuber, Wraya, Galensab, & Herrmann, 1990; 11. Fang, Veitch, Kite, Porter, & Simmonds, 2013; 12. Pop, et al., 2013; 13. Lavola, Karjalainen, & Julkunen-Tiitto, 2012; 14. Wald, Galensa, Herrmann, Grotjahn, & Wray, 1986; 15. Ek, Kartimo, Mattila, & Tolonen, 2006; 16. Riihinena, Gödeckec, & Pauli, 2012; 17. Vvedenskaya, & Vorsa, 2004; 18. Kathirvel, Gong, & Richards, 2009; 19. Mikulic-Petkovsek, Slatnar, Stampar, & Veberic, 2012; 20. Laaksonen, Sandell, Järvinen, & Kallio, 2011; 21. Ma, et al., 2016; 22. Yang, Halttunen, Raimo, Price, & Kallio, 2009; 23. Liu, Kallio, Yang, 2014; 24. Zhang, Xu, Yu, Zhang, & Tang, 2010; 25. Lavola, Karjalainen, & Julkunen-Tiitto, 2012; 26. Veberic, Slatnar, Bizjak, Stampar, & Mikulic-Petkovsek, 2015; 27. Nour, Stampar, Veberic, & Jakopic, 2013; 28. Dinkova, Heffels, Shikov, Weber, Schieber, & Mihalev, 2014; 29. McKay, Chen, Zampariello, & Blumberg, 2015; 30. Liu, Lindstedt, Markkinen, Sinkkonen, Suomela, & Yang, 2014.

Figure 1

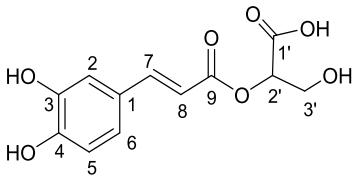
Click here to download Figure(s): Fig. 1.docx

a



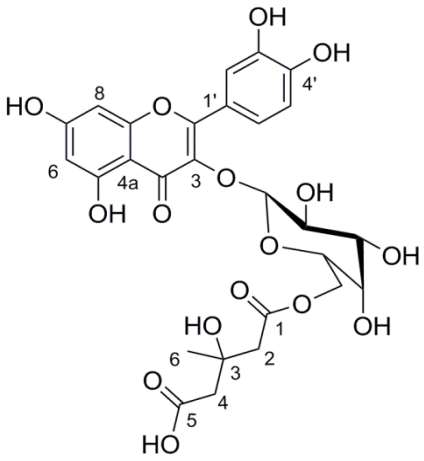
Benzoyl *β*-glucose		^{1}H (δ/ppm)	multiplicity (*J*/Hz)	^{13}C (δ/ppm)
aglycone	1	-	-	131.9
	2	8.09	dd (1.3, 8.2)	132.8
	3	7.53	dd (7.5, 8.2)	131.7
	4	7.68	t (7.5)	137.2
	5	7.53	dd (7.5, 8.2)	131.7
	6	8.09	dd (1.3, 8.2)	132.8
	7	-	-	169.4
glucose	1'	5.73	d (7.8)	98.0
	2'	3.43-3.58	m	72.4-80.3
	3'	3.43-3.58	m	72.4-80.3
	4'	3.43-3.58	m	72.4-80.3
	5'	3.43-3.58	m	72.4-80.3
	6'	3.73	dd (5.2, -12.5)	63,8
		3.88	dd (2.1, -12.5)	

b



Caffeoylglyceric acid	^{1}H (δ/ppm)	multiplicity (*J*/Hz)	^{13}C (δ/ppm)
1	-	-	128.1
2	7.07	d (2.1)	115.3
3	-	-	146.9
4	-	-	149.7
5	6.78	d (8.2)	116.6
6	6.96	dd (2.1, 8.2)	123.1
7	7.64	d (15.9)	147.3
8	6.38	d (15.9)	115.4
9	-	-	169.0
1'	-	-	174.1
2'	5.11	dd (3.5, 6.3)	77.1
3'	3.92	dd (6.3, 12.2)	63.4
	4.00	dd (3.5, 12.2)	

c



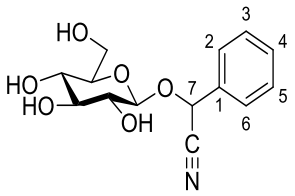
Quercetin 3-*O*-[6''-(3-hydroxy-3-methylglutaroyl)-*β*-galactoside]		^{1}H (δ/ppm)	multiplicity (*J*/Hz)	^{13}C[a] (δ/ppm)
aglycone	2	-	-	157.5
	3	-	-	134.2
	4	-	-	[b]
	4a	-	-	103.8
	5	-	-	[c]
	6	6.22	d (2.1)	98.8
	7	-	-	[c]
	8	6.43	d (2.1)	93.7
	8a	-	-	157.0
	1'		-	121.2
	2'	7.81	d (2.2)	116.5
	3'	-	-	144.9
	4'	-	-	148.6
	5'	6.86	d (8.5)	114.9
	6'	7.62	dd (2.2, 8.5)	121.8
galactose	1	5.09	d (7.8)	104.4
	2	3.80	m	71.8
	3	3.57	dd (9.5, 3.4)	73.7
	4	3.83	m	69.10
	5	3.70	m	73.2
	6	4.12	m	63.2
3-hydroxy-3-methylglutaric acid				
	1	-	-	171.0
	2	2.40	d 14.2	45.5
		2.45	d 14.2	
	3	-	-	69.2
	4	2.35	d 15.2	45.5
		2.45	d 15.2	
	5	-	-	175.7
	6	1.17	s	26.7

a. ^{13}C spectrum was not measured due to very small sample quantity. ^{13}C chemical shifts were obtained from HSQC and HMBC spectra.

b. No HMBC correlation and thus could not be determined.

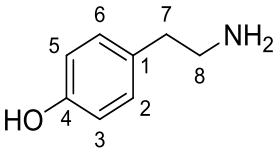
c. The ^{13}C chemical shift of carbon 5 or 7 based on HMBC correlation was 161.1. No HMBC correlation to the other of the carbons could be detected.

d



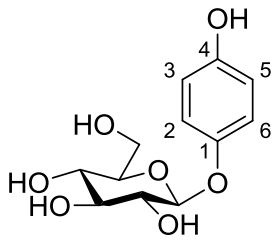
Prunasin		^{1}H (δ/ppm)	multiplicity (*J*/Hz)	^{13}C (δ/ppm)
aglycone	1	-	-	136.1
	2	7.58	m	130.6
	3	7.49	m	132.2
	4	7.49	m	133.2
	5	7.49	m	132.2
	6	7.58	m	130.6
	7	5.90	s	70.9
	8	-	-	121.5
glucose	1'	4.37	d (7.4)	104.1
	2'	3.28–3.36	m	72.6-79.8
	3'	3.28–3.36	m	72.6-79.8
	4'	3.28–3.36	m	72.6-79.8
	5'	3.28–3.36	m	72.6-79.8
	6'	3.73	dd (5.7, -12.2)	64.2
		3.91	dd (2.3, -12.2)	

e



Tyramine		^{1}H (δ/ppm)	multiplicity (*J*/Hz)	^{13}C (δ/ppm)
	1	-	-	130.9
	2	7.13	d (8.4)	132.9
	3	6.81	d (8.4)	118.6
	4	-	-	158.7
	5	6.81	d (8.4)	118.6
	6	7.13	d (8.4)	132.9
	7	2.88	t (8.0)	35.2
	8	3.14	t (8.0)	44.0

f

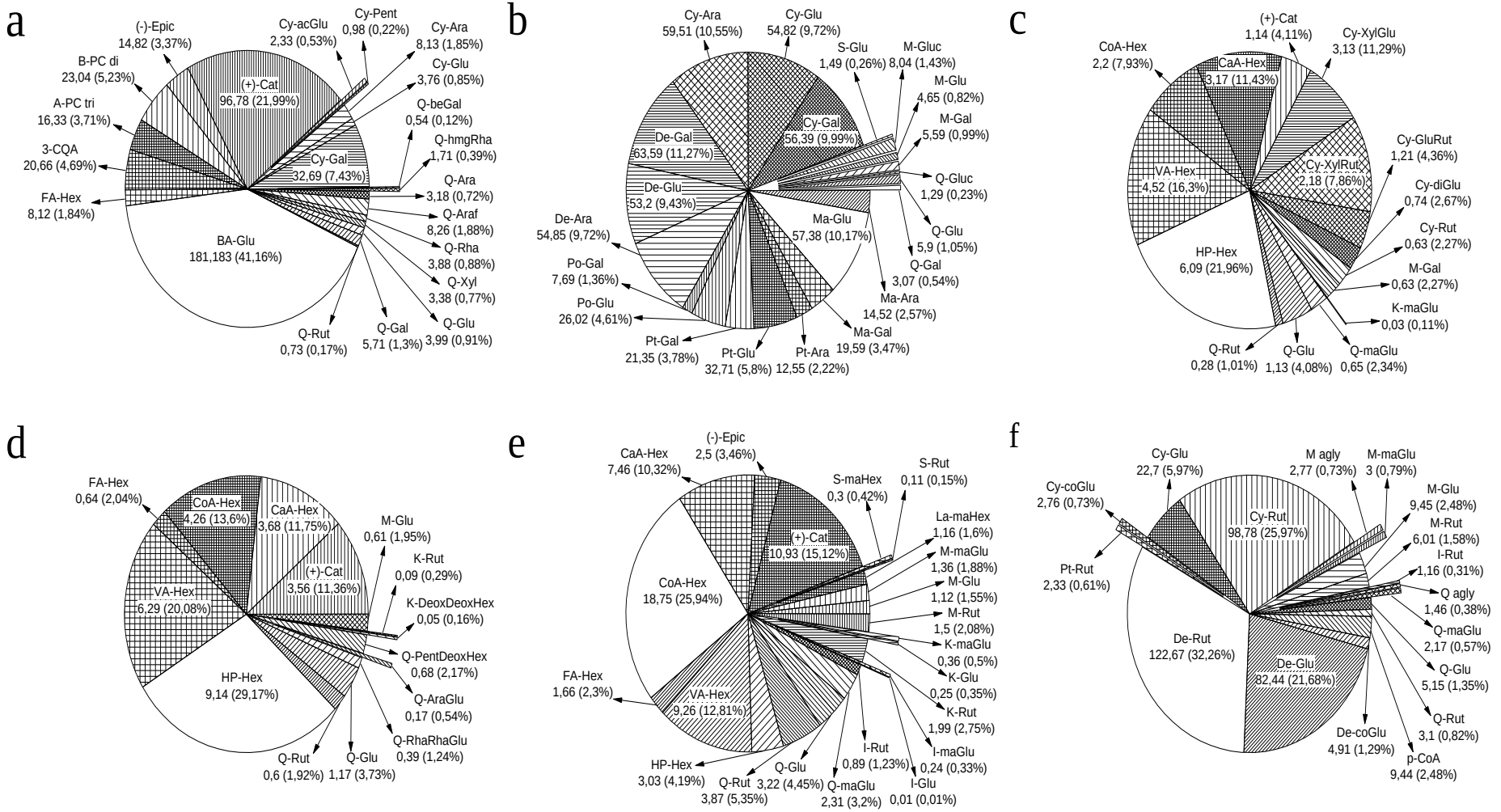


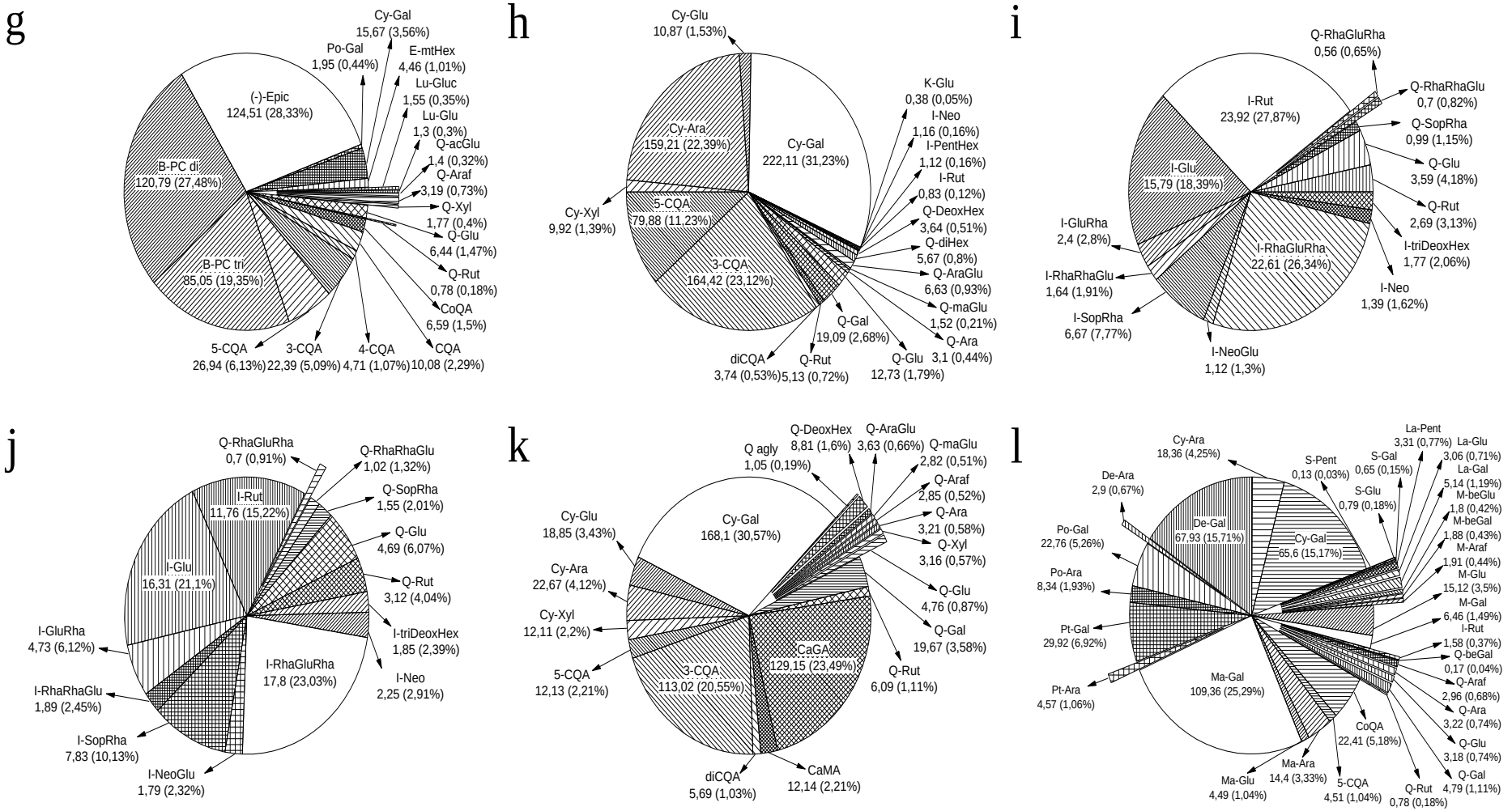
***β*-p-arbutin**		^{1}H (δ/ppm)	multiplicity (*J*/Hz)	^{13}C (δ/ppm)
aglycone	1	-	-	154.0
	2	7.00	d (8.9)	121.4
	3	6.77	d (8.9)	118.8
	4	-	-	155.0
	5	6.77	d (8.9)	118.8
	6	7.00	d (8.9)	121.4
glucose	1'	4.82	d (7.6)	105.1
	2'	3.48	m	76.5
	3'	3.53	m	79.3
	4'	3.45	m	72.9
	5'	3.45	m	79.5
	6'	3.74	br d (-12.0)	64.0
		3.89	br d (-12.0)	

Fig. 1. Structural information of compounds identified by NMR. Information of compounds b, d, e and f were collected from the full NMR spectra of the extracts (Chapter 2.4, Supplemental Figure 1). Compounds a, c and d were isolated by HPLC before NMR analysis (Chapter 2.6).

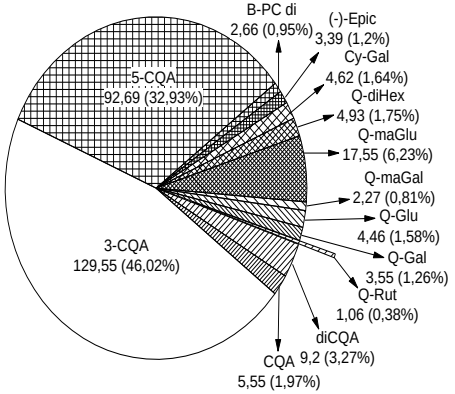
Figure 2

Click here to download Figure(s): Fig. 2.docx




g
Cy-Gal
15,67 (3,56%)
Po-Gal
1,95 (0,44%)
E-mtHex
4,46 (1,01%)
Lu-Gluc
1,55 (0,35%)
Lu-Glu
1,3 (0,3%)
Q-acGlu
1,4 (0,32%)
Q-Araf
3,19 (0,73%)
Q-Xyl
1,77 (0,4%)
Q-Glu
6,44 (1,47%)
Q-Rut
0,78 (0,18%)
CoQA
6,59 (1,5%)
CQA
10,08 (2,29%)
4-CQA
4,71 (1,07%)
3-CQA
22,39 (5,09%)
5-CQA
26,94 (6,13%)
B-PC tri
85,05 (19,35%)
B-PC di
120,79 (27,48%)
(-)-Epic
124,51 (28,33%)
h
Cy-Glu
10,87 (1,53%)
K-Glu
0,38 (0,05%)
I-Neo
1,16 (0,16%)
I-PentHex
1,12 (0,16%)
I-Rut
0,83 (0,12%)
Q-DeoxHex
3,64 (0,51%)
Q-diHex
5,67 (0,8%)
Q-AraGlu
6,63 (0,93%)
Q-maGlu
1,52 (0,21%)
Q-Ara
3,1 (0,44%)
Q-Glu
12,73 (1,79%)
Q-Rut
5,13 (0,72%)
diCQA
3,74 (0,53%)
Q-Gal
19,09 (2,68%)
3-CQA
164,42 (23,12%)
5-CQA
79,88 (11,23%)
Cy-Xyl
9,92 (1,39%)
Cy-Ara
159,21 (22,39%)
Cy-Gal
222,11 (31,23%)
i
Q-RhaGluRha
0,56 (0,65%)
Q-RhaRhaGlu
0,7 (0,82%)
Q-SopRha
0,99 (1,15%)
Q-Glu
3,59 (4,18%)
Q-Rut
2,69 (3,13%)
I-triDeoxHex
1,77 (2,06%)
I-Neo
1,39 (1,62%)
I-NeoGlu
1,12 (1,3%)
I-SopRha
6,67 (7,77%)
I-RhaRhaGlu
1,64 (1,91%)
I-GluRha
2,4 (2,8%)
I-RhaGluRha
22,61 (26,34%)
I-Glu
15,79 (18,39%)
I-Rut
23,92 (27,87%)
j
Q-RhaGluRha
0,7 (0,91%)
Q-RhaRhaGlu
1,02 (1,32%)
Q-SopRha
1,55 (2,01%)
Q-Glu
4,69 (6,07%)
Q-Rut
3,12 (4,04%)
I-triDeoxHex
1,85 (2,39%)
I-Neo
2,25 (2,91%)
I-RhaGluRha
17,8 (23,03%)
I-NeoGlu
1,79 (2,32%)
I-SopRha
7,83 (10,13%)
I-RhaRhaGlu
1,89 (2,45%)
I-GluRha
4,73 (6,12%)
I-Glu
16,31 (21,1%)
I-Rut
11,76 (15,22%)
k
Q agly
1,05 (0,19%)
Q-DeoxHex
8,81 (1,6%)
Q-AraGlu
3,63 (0,66%)
Q-maGlu
2,82 (0,51%)
Q-Araf
2,85 (0,52%)
Q-Ara
3,21 (0,58%)
Q-Xyl
3,16 (0,57%)
Q-Glu
4,76 (0,87%)
Q-Gal
19,67 (3,58%)
Q-Rut
6,09 (1,11%)
CaMA
12,14 (2,21%)
diCQA
5,69 (1,03%)
CaGA
129,15 (23,49%)
3-CQA
113,02 (20,55%)
5-CQA
12,13 (2,21%)
Cy-Xyl
12,11 (2,2%)
Cy-Ara
22,67 (4,12%)
Cy-Glu
18,85 (3,43%)
Cy-Gal
168,1 (30,57%)
l
Cy-Ara
18,36 (4,25%)
La-Pent
3,31 (0,77%)
La-Glu
3,06 (0,71%)
La-Gal
5,14 (1,19%)
M-beGlu
1,8 (0,42%)
M-beGal
1,88 (0,43%)
M-Araf
1,91 (0,44%)
M-Glu
15,12 (3,5%)
M-Gal
6,46 (1,49%)
I-Rut
1,58 (0,37%)
Q-beGal
0,17 (0,04%)
Q-Araf
2,96 (0,68%)
Q-Ara
3,22 (0,74%)
Q-Glu
3,18 (0,74%)
Q-Gal
4,79 (1,11%)
Q-Rut
0,78 (0,18%)
5-CQA
4,51 (1,04%)
CoQA
22,41 (5,18%)
Ma-Ara
14,4 (3,33%)
Ma-Glu
4,49 (1,04%)
Ma-Gal
109,36 (25,29%)
Pt-Ara
4,57 (1,06%)
Pt-Gal
29,92 (6,92%)
Po-Ara
8,34 (1,93%)
Po-Gal
22,76 (5,26%)
De-Ara
2,9 (0,67%)
De-Gal
67,93 (15,71%)
S-Pent
0,13 (0,03%)
S-Gal
0,65 (0,15%)
S-Glu
0,79 (0,18%)
Cy-Gal
65,6 (15,17%)

m



n

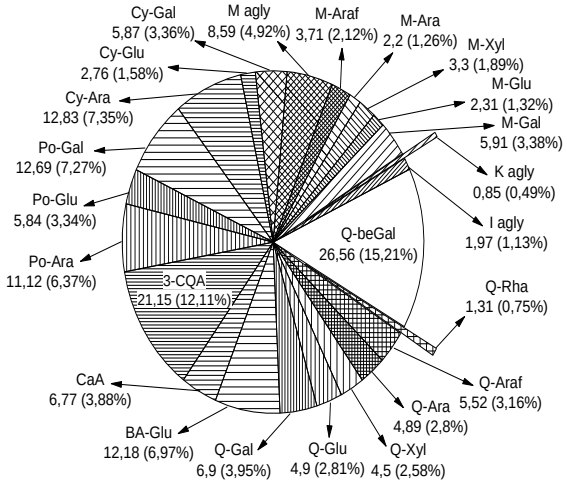
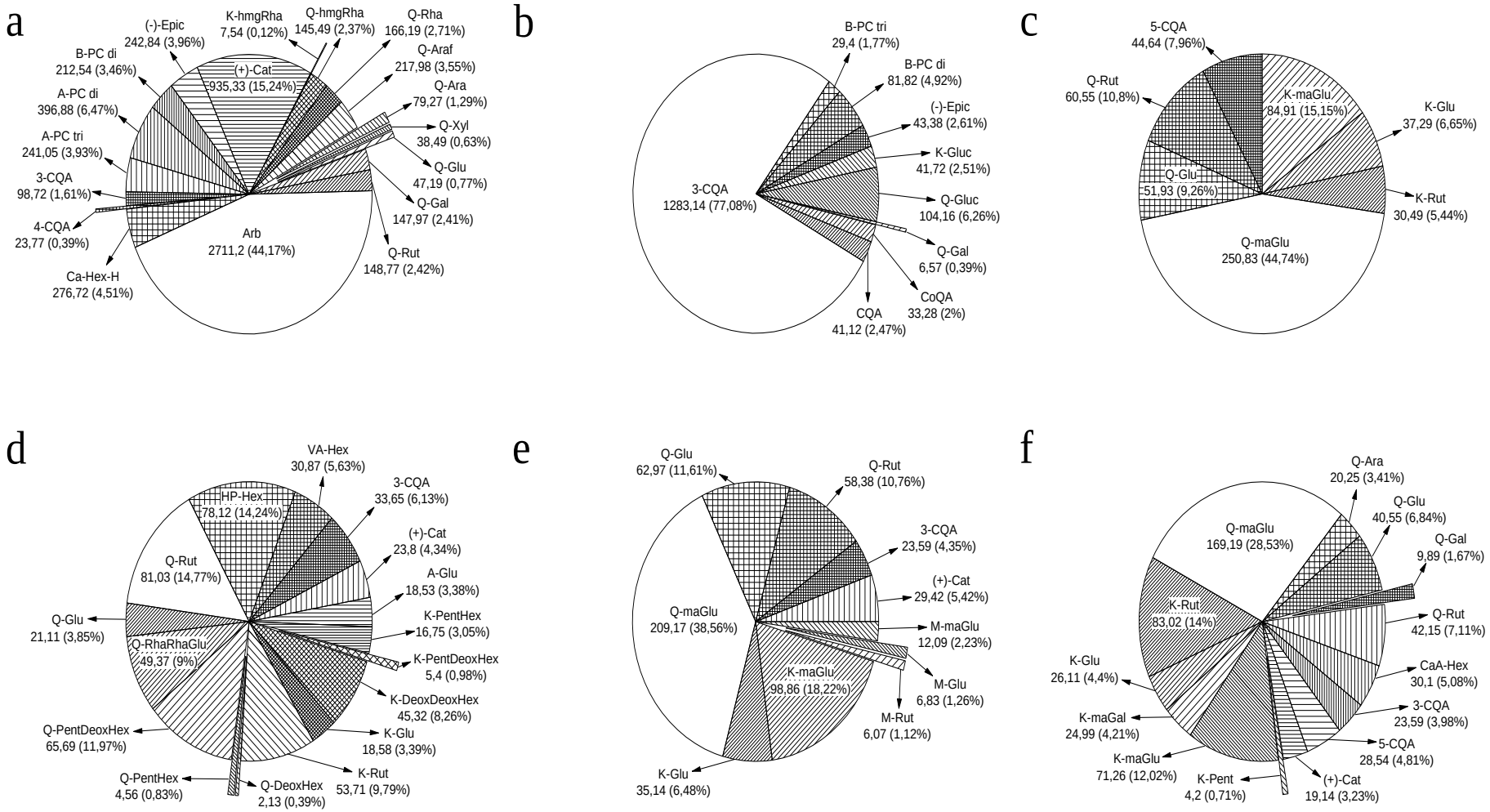


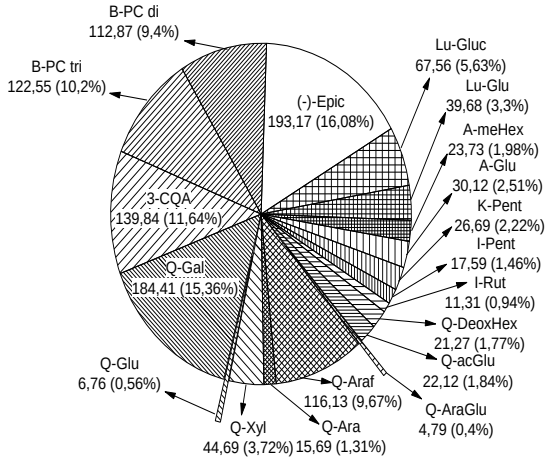
Fig. 2. Concentration (mg/100 g, fresh weight) and percentage of phenolic composition in berries: a. lingonberry (total content of phenolics: 440 mg/100 g fresh weight); b. bilberry (564); c. red currant (28); d. white currant (31); e. green currant (72); f. black currant press cake (380); g. hawthorn (440 mg/100 g); h. chokeberry (711); i. sea buckthorn ‘Terhi’ (86); j. sea buckthorn ‘Tytti’ (77); k. saskatoon berry (550); l. crowberry (432); m. rowanberry (281); n. cranberry press cake (148).

Figure 3

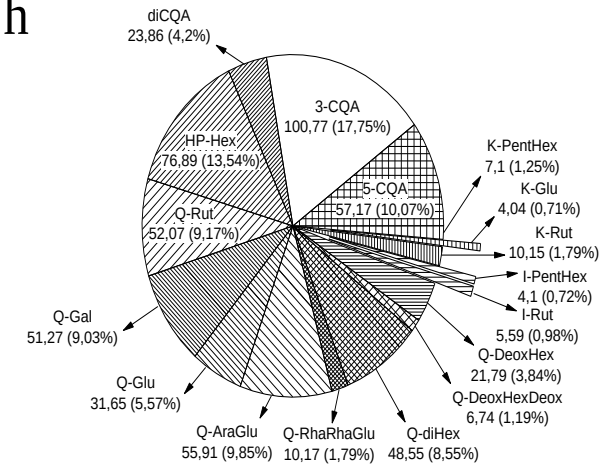
Click here to download Figure(s): Fig. 3.docx



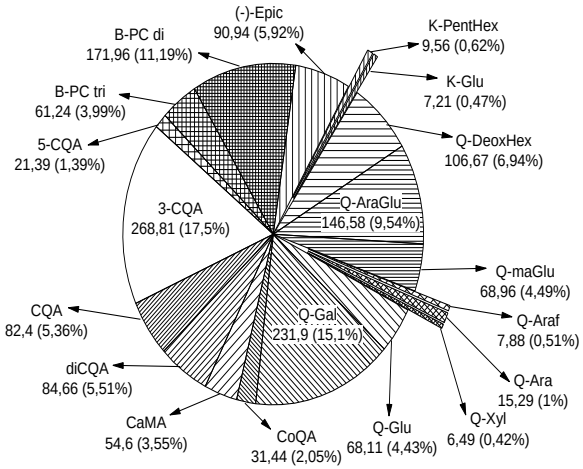
g


B-PC di
112,87 (9,4%)
B-PC tri
122,55 (10,2%)
(-)-Epic
193,17 (16,08%)
Lu-Gluc
67,56 (5,63%)
Lu-Glu
39,68 (3,3%)
A-meHex
23,73 (1,98%)
A-Glu
30,12 (2,51%)
K-Pent
26,69 (2,22%)
I-Pent
17,59 (1,46%)
I-Rut
11,31 (0,94%)
Q-DeoxHex
21,27 (1,77%)
Q-acGlu
22,12 (1,84%)
Q-AraGlu
4,79 (0,4%)
3-CQA
139,84 (11,64%)
Q-Gal
184,41 (15,36%)
Q-Glu
6,76 (0,56%)
Q-Araf
116,13 (9,67%)
Q-Xyl
44,69 (3,72%)
Q-Ara
15,69 (1,31%)

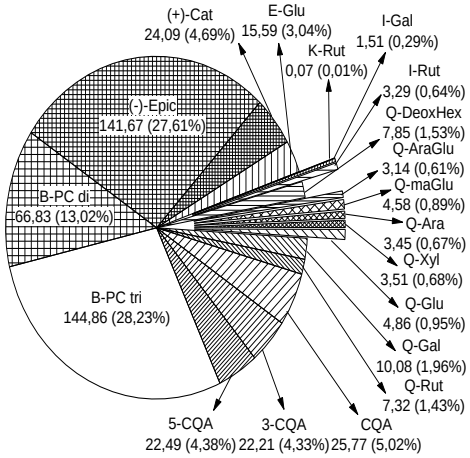
h


diCQA
23,86 (4,2%)
3-CQA
100,77 (17,75%)
HP-Hex
76,89 (13,54%)
5-CQA
57,17 (10,07%)
Q-Rut
52,07 (9,17%)
K-PentHex
7,1 (1,25%)
K-Glu
4,04 (0,71%)
K-Rut
10,15 (1,79%)
I-PentHex
4,1 (0,72%)
I-Rut
5,59 (0,98%)
Q-DeoxHex
21,79 (3,84%)
Q-DeoxHexDeox
6,74 (1,19%)
Q-Gal
51,27 (9,03%)
Q-Glu
31,65 (5,57%)
Q-AraGlu
55,91 (9,85%)
Q-RhaRhaGlu
10,17 (1,79%)
Q-diHex
48,55 (8,55%)

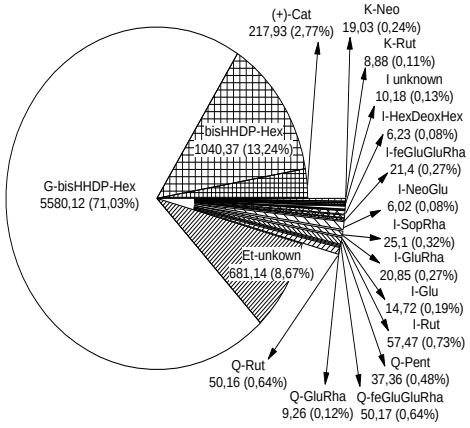
i


(-)-Epic
90,94 (5,92%)
B-PC di
171,96 (11,19%)
K-PentHex
9,56 (0,62%)
K-Glu
7,21 (0,47%)
B-PC tri
61,24 (3,99%)
Q-DeoxHex
106,67 (6,94%)
5-CQA
21,39 (1,39%)
3-CQA
268,81 (17,5%)
Q-AraGlu
146,58 (9,54%)
Q-maGlu
68,96 (4,49%)
Q-Araf
7,88 (0,51%)
CQA
82,4 (5,36%)
Q-Gal
231,9 (15,1%)
Q-Ara
15,29 (1%)
diCQA
84,66 (5,51%)
Q-Xyl
6,49 (0,42%)
CaMA
54,6 (3,55%)
CoQA
31,44 (2,05%)
Q-Glu
68,11 (4,43%)

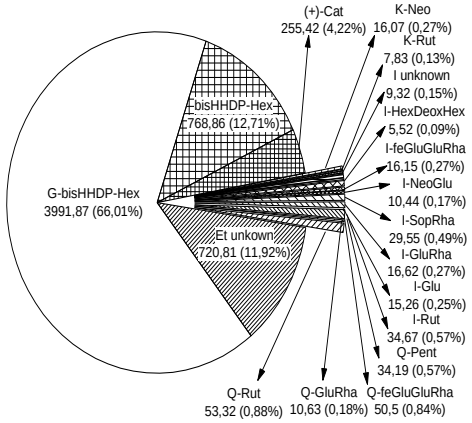
j


(+)-Cat
24,09 (4,69%)
E-Glu
15,59 (3,04%)
I-Gal
1,51 (0,29%)
K-Rut
0,07 (0,01%)
I-Rut
3,29 (0,64%)
(-)-Epic
141,67 (27,61%)
Q-DeoxHex
7,85 (1,53%)
Q-AraGlu
3,14 (0,61%)
Q-maGlu
4,58 (0,89%)
B-PC di
66,83 (13,02%)
Q-Ara
3,45 (0,67%)
Q-Xyl
3,51 (0,68%)
B-PC tri
144,86 (28,23%)
Q-Glu
4,86 (0,95%)
Q-Gal
10,08 (1,96%)
Q-Rut
7,32 (1,43%)
5-CQA
22,49 (4,38%)
3-CQA
22,21 (4,33%)
CQA
25,77 (5,02%)

k


(+)-Cat
217,93 (2,77%)
K-Neo
19,03 (0,24%)
K-Rut
8,88 (0,11%)
I unknown
10,18 (0,13%)
bisHHDP-Hex
1040,37 (13,24%)
I-HexDeoxHex
6,23 (0,08%)
I-feGluGluRha
21,4 (0,27%)
G-bisHHDP-Hex
5580,12 (71,03%)
I-NeoGlu
6,02 (0,08%)
I-SopRha
25,1 (0,32%)
Et-unkown
681,14 (8,67%)
I-GluRha
20,85 (0,27%)
I-Glu
14,72 (0,19%)
I-Rut
57,47 (0,73%)
Q-Pent
37,36 (0,48%)
Q-Rut
50,16 (0,64%)
Q-GluRha
9,26 (0,12%)
Q-feGluGluRha
50,17 (0,64%)

l


(+)-Cat
255,42 (4,22%)
K-Neo
16,07 (0,27%)
K-Rut
7,83 (0,13%)
I unknown
9,32 (0,15%)
bisHHDP-Hex
768,86 (12,71%)
I-HexDeoxHex
5,52 (0,09%)
I-feGluGluRha
16,15 (0,27%)
G-bisHHDP-Hex
3991,87 (66,01%)
I-NeoGlu
10,44 (0,17%)
I-SopRha
29,55 (0,49%)
Et unkown
720,81 (11,92%)
I-GluRha
16,62 (0,27%)
I-Glu
15,26 (0,25%)
I-Rut
34,67 (0,57%)
Q-Pent
34,19 (0,57%)
Q-Rut
53,32 (0,88%)
Q-GluRha
10,63 (0,18%)
Q-feGluGluRha
50,5 (0,84%)

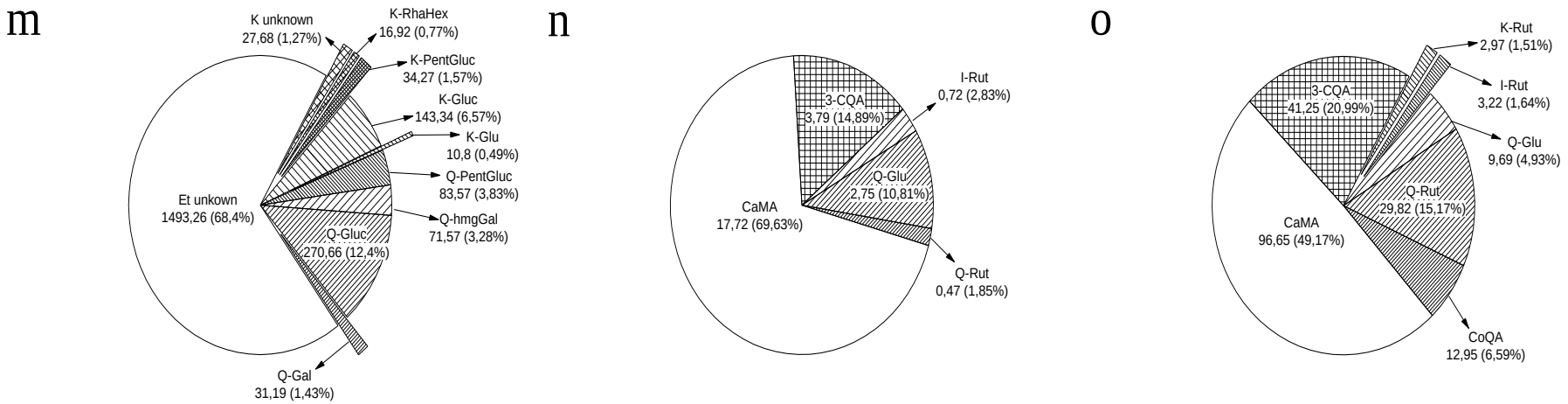


Fig. 3. Concentrations (mg/100 g, fresh weight) and percentage of phenolic composition in leaves and saskatoon branch: a. lingonberry leaf (total content of phenolics: 6138 mg/100 g fresh weight); b. bilberry leaf (1665); c. red currant leaf (561); d. white currant leaf (549); e. green currant leaf (543); f. black currant leaf (594); g. hawthorn leaf (1201); h. chokeberry leaf (568); i. saskatoon leaf (1536); j. saskatoon branch (513); k. sea buckthorn leaf 'Terhi' (7856); l. sea buckthorn leaf 'Tytti' (6047); m. raspberry leaf (2183); n. nettle (October 2013, 25); o. nettle (July 2013, 197).

Supplementary Figure 1

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Supplementary Figure 2

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