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Compositional diversity among blackcurrant (*Ribes nigrum*) cultivars originating from European countries

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ABSTRACT: Berries representing 21 cultivars of blackcurrant were analyzed using liquid chromatographic, gas chromatographic, and mass spectrometric methods coupled with multivariate models. This study pinpointed compositional variation among cultivars of different origins cultivated in the same location during two seasons. The chemical profiles of blackcurrants varied significantly among cultivars and growing years. The key differences among cultivars of Scottish, Lithuanian, and Finnish origin were in the contents of phenolic acids (23 vs. 16 vs. 19 mg/100 g on average, respectively), mainly as 5-*O*-caffeoylquinic acid, 4-*O*-coumaroylglucose, (*E*)-coumaroyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile, and 1-*O*-feruloylglucose. The Scottish cultivars were grouped based on the 3-*O*-glycosides of delphinidin and cyanidin, as were the Lithuanian cultivars. Among the Finnish samples, the content of myricetin 3-*O*-glycosides, 4-*O*-caffeoylglucose, 1-*O*-coumaroylglucose, and 4-*O*-coumaroylglucose were significantly different between the two green-fruited cultivars and the black-fruited cultivars. The samples from the studied years differed in the content of phenolic acid derivatives, quercetin glycosides, monosaccharides and citric acid.

KEYWORDS: blackcurrant, cultivar, organic acids, phenolic compounds, sugars

INTRODUCTION

Horticultural plants have been used for food, fiber, biofuel, medicine, and other products to sustain and enhance human life in the recent years.[1-3] As a species of family *Grossulariaceae*, blackcurrants (*Ribes nigrum*) are rich source of bioactive metabolites and flavor compounds, including sugars, acids, and phenolic compounds.[4-7] Some of the compounds have significant physiological effects on maintenance of cardiovascular health, restriction of cancer growth, control of blood glucose levels, and other physiological functions in *in vitro* models.[8,9] This leads to a commercial exploitation of blackcurrant as food products and nutritional supplements.

The contents and profiles of bioactive metabolites and flavor compounds are not present constantly in *R. nigrum* berries. A number of previous studies have confirmed that environmental factors affect the chemical composition.[10-12] For example, in the berries of the cultivar 'Vertti', the concentration of phenolic compounds, especially the conjugates of hydroxycinnamic acids, was dependent on the latitude of the growing site.[10] Strong correlation with temperature and radiation was found in the content of some phenolic compounds such as delphinidin-3-*O*-glucoside, delphinidin-3-*O*-rutinoside, and myricetin-3-*O*-glucoside in 'Melalahti', 'Mortti' and 'Ola'.[11] The genotype is another major factor influencing chemical profile of *R. nigrum* berries. Vagiri *et al.* studied blackcurrant berries of Scottish, Swedish, and Russian origins, revealing large variations in polyphenols, ascorbic acid, and soluble sugars among the genotypes.[13] Mikulic-Petkovsek found that the contents of acids, sugars, and main groups of phenolics varied significantly during fruit ripening among blackcurrant cultivars 'Rosenthal', 'Tenah', and 'Titania'.[14] Similarly, differences were observed among the cultivars 'Titania', 'Triton', 'Tsema', and 'Cacanska crna'.[15] The impact of genotype can also be seen in juice processing where the juice produced from a single cultivar maintains its typical sensory characteristics during the process.[6]

Due to extensive industrial demand, new cultivars of blackcurrant are always requested. The main goal of commercial breeding of new cultivars usually focuses on the adaptation of plants to abiotic and biotic environment, as well as their cropping potential.[16-17] For breeders, breeding is a long and exacting work, making use of previous breeding results and even the achievements of the previous breeders' generations. It is thus of high importance for breeders to have better knowledge about the fruit quality characteristics of cultivars. Since some common ancestors are typically used in cultivar development, it is even possible that there are some limitations related to fruit quality in breeding populations.

Likewise, food industry needs fruits with specific properties to meet the requirement of processing or to reach the target quality of final products. These may not be achieved by using cultivars traditionally grown by its raw material producers. The chemical composition of blackcurrant fruits has been traditionally less emphasized when new cultivars are selected. The previous studies on chemical profiles of blackcurrants have focused on either a limited number of compounds or only a few cultivars. Therefore, it is necessary to investigate systematically the compositional difference among a collection of blackcurrant cultivars that are bred and cultivated in different countries. The results of our study provide new knowledge to help breeders, trade, and food industry to ensure success in providing targeted quality of blackcurrant fruit and fruit products.

In this study, we investigated and compared the composition of twenty-one cultivars of blackcurrants originating from five different countries. All cultivars were planted in 2009 at the same location and treated with the same cultivating practice. Samples collected during two consecutive years were analyzed in order to get on an idea of the possible seasonal variation. The variations in the compositions of various phenolic compounds, simple sugars, and acids were determined using liquid chromatographic (LC), gas chromatographic (GC)

and mass spectrometric (MS) methods, followed by comparison of datasets with partial least squares (PLS) regression models. Our aim was to pinpoint the main groups or individual compounds separating different cultivars and origins. This knowledge will assist plant breeding as well as providing guidance for food industry in selection of raw-materials and farmers in selecting cultivars.

MATERIALS AND METHODS

Materials. Blackcurrant cultivars originating from Scotland (9 cultivars), Lithuania (5 cultivars), Latvia (1 cultivar), Poland (1 cultivar), and Finland (5 cultivars) were cultivated in the test site of Natural Resources Institute (Luke) in Piikkiö, Kaarina, southwest Finland (latitude 60°23′ N, longitude 22°33′ E, altitude ca. 5 m). The propagation material of plants was provided by the breeding institute of each cultivar, to guarantee the true-to-type of the cultivars. One-year old transplants were planted in 2009 in three rows, with a distance of 4 m between rows and 1 m between plants within a row. Two plants of each cultivar were planted in a plot randomized in each row. Berries for the analyses were sampled from the total harvest of each plot in August 2014 and 2015, each representing one replicate sample of each cultivar. The soil was silt moraine rich in organic matter. Irrigation via a trickle tape, fertilization and other cultivation methods were according to the Finnish standard guidelines.[18] The harvesting time of each cultivar was defined by experienced horticulturist, the definition being based on the color, flavor, and structure of optimally ripe berries. The samples collected in year 2014 were firstly stored in a freezer at -70 °C for one year, and then transferred to -20 °C together with the samples harvest in 2015 for 5 months. All frozen samples were then delivered from Luke to University of Turku, and stored at -20 °C for a maximum period of 15 months until all analyses were completed. The information of the

samples is shown in **Supplemental Table 1**, including cultivar names, origin countries, and harvesting dates.

Weather conditions. Data on climatic conditions were collected in the meteorological station in the Luke Kaarina test site and provided by the Finnish Meteorological Institute (Helsinki, Finland), to give information of the climatic differences between the fruit ripening periods of the two years. The main climatic factors with the one-month time interval during July 20–August 20 are shown in **Supplemental Table 4**. The time interval was chosen to cover the harvesting period of all cultivars in 2014 and all but two very late cultivars in 2015, and at least 12 days preceding the earliest harvest date.

Dry matter content. Approximately 5 g of currant samples were weight accurately, and cut with blade in watch-glass. The residue on the blade was rinsed into the watch-glass with Milli-Q water. The samples were dried in the oven (Oy Santasalo-Sohlberg Ab, Helsinki, Finland) at 105 °C overnight until their weights reached a constant value.

Phenolic compounds. Phenolic compounds were identified using a Waters Acquity Ultra performance liquid chromatography (UPLC) system equipped with 2996 DAD detector, an electrospray ionization interface (ESI) and a Waters Quattro Premier mass spectrometer (Waters Corp., Milford, MA). All phenolics were characterized by comparing LC retention time and typical mass fragments with reference compounds and literature.[6,19-29] Mass spectrometry was set in both negative- and positive-ion mode, the condition of which was reported in our previous study.[20]

Two methods were applied for analysis based on the types of phenolic compounds. For

anthocyanins, 5 g of frozen berries were crushed into slurry and extracted with 15 mL of acidic methanol (MeOH/HCl 99:1), followed by ultra-sonication (10 min) and centrifuge (4420× g for 10 min). The extraction was carried out three times. The three supernatants were combined, and the total volume was set to 50 mL with acidic methanol. The samples were filtered through a 0.2 μm syringe filter before UPLC-DAD-ESI-MS analysis (Waters Corp., Milford, MA, USA). The analysis of anthocyanins was conducted according to the method previously reported by Mäkilä and co-workers.[19] The signal of anthocyanins in the LC analyses was monitored at the wavelength of 520 nm.

Other phenolic compounds were extracted from crushed materials (15 g) with 10 mL of ethyl acetate. Ultra-sonication (15 min) and centrifuge (4420 × g for 15 min) were applied in the four-time extraction. The combined supernatant was evaporated at 36 °C; the residue was dissolved with 3 mL of methanol, and filtered through a 0.2 μm syringe filter. Liquid chromatographic separation was performed with a Phenomenex Aeris peptide XB-C18 column (150 × 4.60 mm, 3.6 μm, Torrance, CA) at room temperature. The injection volume was 10 μL and the total flow was kept at 1 mL/min. The mobile phase was a combination of Milli-Q water (A) and acetonitrile (B), both containing 0.1% (v/v) of formic acid. The gradient applied was: 0–15 min with 8-10% solvent B, 15–20 min with 10–13% B, 20–25 min with 13–16% B, 25–30 min with 16–18% B, 30–35 min with 18–20% B, 35–40 min with 20–22% B, 40–45 min with 22–25% B, 45–50 min with 25–60% B, 50–55 min with 60–8% B, 55–57 min with 8% B. The chromatograms were recorded at three different wavelengths (360 nm for flavonols, 320 nm for phenolic acids, and 280 nm for flavan-3-ols and other phenolic compounds).

The quantification of the phenolics was performed using a Shimadzu LC-10AT liquid chromatograph system, coupled with a SPD-M20A VP photodiode array (Shimadzu Corp., Kyoto, Japan). The chromatographic conditions were the same as in the corresponding

qualitative analyses. The concentration of the compounds identified was determined using an external standard method as described previously.[20] The compounds lacking corresponding reference standards were quantified by the calibration curves of compounds with closest structures. For instance, cyanidin 3-*O*-(6"-coumaroyl)-glucoside was quantified by the calibration curve of cyanidin 3-*O*-glucoside ($y = 3\times10^{-8}\,x + 0.0026$, $R^2 = 0.9990$). The detail information of external standards is given in Supplemental Table 6.

Sugars and simple organic acids. 15 g of frozen berries were crushed with a T25 digital Ultra-Turrax (IKA Werke GmbH & Co. KG, Staufen im Breisgau, Germany) and extracted with 10 mL of Milli-Q water at room temperature. The extraction was assisted with ultra-sonication (15 min) and centrifuge (4420× g for 15 min). After the supernatant was collected, the residue was extracted with the same procedure three times. The supernatants from the four times of extraction were combined and diluted with Milli-Q water to a final volume of 50 mL. Sugars and simple organic acids in the samples were analyzed as trimethylsilyl (TMS) derivatives by Shimadzu GC-2010 equipped with flame ionization detector (Shimadzu corp., Kyoto, Japan). The compounds were identified based on the retention time of reference standards. A mixed internal standard, consisting of sorbitol (for sugars) and tartaric acid (for acids) was used for quantification. The methods for preparation of samples and standards, as well as gas chromatographic conditions, were the same as described in the previous research.[12]

Statistical Analyses. The quantitative analyses of chemical compounds were performed in triplicates. The results were calculated on the base of dry weight (mg/g or 100 g of berries) and expressed as mean ± standard deviation (SD). Partial least squares (PLS) regression with full cross validation was applied to determine the correlation between chemical profile and

cultivar/country of origin/growing year by using Unscrambler 10.4 (Camo Process AS, Oslo, Norway). PLS models were established with the concentrations of compounds as the predictors (X-data), and the cultivars (and other factors listed above) as the responses (Y-data).

RESULTS AND DISCUSSION

Altogether, 63 chemical compounds were identified from blackcurrant berries, primarily as anthocyanins (15 compounds), flavonols (19), flavan-3-ols (4), phenolic acid derivatives (14), organic acids (4) and sugars (6). The qualitative results and chromatographs are given in **Table 1** and **Supplemental Figure 1**, respectively. In accordance with previous study,[30] most of phenolic compounds present in blackcurrants were anthocyanins, flavonols, flavan-3-ols, and the derivatives of hydroxycinnamic acids (caffeic acid, coumaric acid, and ferulic acid). In addition to delphinidin and cyanidin derivatives as the dominant anthocyanins in the berries, the glycosides of petunidin (peak 5&6), pelargonidin (peak 8&9), peonidin (peak 10&11), and malvidin (peak 12&13) were detected and confirmed based on the typical MS fragmentations. These minor anthocyanins were not reported in previous studies.[22,23] Presence of anthocyanins was not the only difference between black and green cultivars. Some flavonols present in black cultivars were not found in the two green-fruited cultivars, such as myricetin 3-*O*-arabinoside (peak 19), quercetin 3-*O*-galactoside (peak 22), quercetin 3-*O*-arabinoside (peak 24), isorhamnetin 3-*O*-(6"-malonyl)-galactoside (peak 31), myricetin-hexoside-deoxyhexoside (peak 32), and myricetin aglycone (peak 29). Organic acids in blackcurrants were characterized as malic acid, citric acid, quinic acid, and ascorbic acid. The main sugars in blackcurrants were fructose, glucose, and sucrose.

Quantification of the compounds. Sum content of phenolics ranged from 598 to 2798 mg/100g in black cultivars and from 47 to 104 mg/100 g in green ones (**Supplemental Table 2**). It has been discussed previously that the absence of anthocyanins resulted in the lowest amount of total phenolics in green cultivars.[31] Among all black cultivars, the total content of anthocyanin was 1501 ± 587 mg/100 g, which was lower than previously detected by Mattila *et al*. (2057 ± 442 mg/100 g dry weight, DW) in 32 Finnish blackcurrant cultivars in a germplasm collection of mainly traditional cultivars.[32] Nour *et al*. reported that glycosides of cyanidin and delphinidin (3-*O*-glucoside and 3-*O*-rutinoside) accounted for 92–97% of total anthocyanins in blackcurrants.[33] Similar percentages were found in the current study. Anthocyanins formed the dominating groups of the phenolics in black-fruited samples, mainly as glycosylated delphinidin (34–66% of sum content of phenolics) and cyanidin (31–52%). The total content of flavonols was 18–60 mg/100 mg dry weight, accounting for 1–6% of sum content of phenolics in black cultivars, and 37–39% in green ones. The difference between black and green cultivars was also shown in the profile of flavonols. In accordance with the results published by Mikkonen *et al*.,[34] myricetin glycosides was the dominant group of flavonols in the black cultivars studied; however, total content of quercetin glycosides was 6–8 times higher than that of myricetin glycosides in the green cultivars 'Vilma' and 'Venny'.

For phenolic acids, the conjugates of coumaric acids (47–74% of total phenolic acid derivatives) were the major components in the most of the cultivars, followed by caffeic acid (17–40%) and ferulic acid (9–20%); however, the cultivars 'Ben Tron' and 'Joniniai' contained more derivatives of caffeic acids and less of coumaric acids in both years. Moreover, the monomers of flavan-3-ols were found at a total content close to 10–20 mg/100 g.

Although the contents of simple organic acids significantly differed among the cultivars, citric acid accounted for 75–97% of the total content of simple acids (**Supplemental table 3**) in accordance with previous report.[35] It was followed by malic acid representing 3–20% of total simple acids. The highest values of ascorbic acid were found in 'Tisel' (2.0–2.5 mg/g), 'Joniniai' (2.2–2.5 mg/g), and 'Ben Tirran' (1.7–2.3 mg/g); however, in Finnish black cultivars, ascorbic acid was found at considerably low contents ranging from 0.2 to 0.6 mg/g. A small quantity of quinic acid was detected in all the samples. As the dominating sugars in all blackcurrant cultivars studied, fructose and glucose contributed 48–60% and 38–47% of total content of sugars, respectively. The concentration of fructose was higher than that of glucose in all the cultivars. Compared to fructose and glucose, sucrose was present at a lower level in the black-fruited currants as suggested by Woznicki.[36] In this study, 'Dainiai' showed significantly higher sucrose content (12 mg/g on average) than other cultivars studied. The contents of simple organic acids and sugars found in the samples in the current study deviated considerably from the levels reported in some blackcurrant cultivars studied in previous research studies.[13,35] This difference was likely due to the different genetic background of the cultivars included in these studies. Also, the growth locations were different in these studies; therefore the environmental factors may have contributed to the difference observed.

Comparison of blackcurrant cultivars growing in different years. A large and significant variation in chemical variables was observed within each cultivar between years 2014 and 2015. For phenolic compounds, two green cultivars presented significantly lower sum-content of phenolics than the black cultivars. A newly bred Scottish sample, 'S 18/2/23', was also low in phenolics (598–745 mg/100 g of dry berries) in both years. Since annual deviation was seen likely due to the response of plants to the environment, a PLS regression model was

used to find the distribution of individual compounds in different years. Regarding to phenolic compounds, 78% of the chemical variables explained 89% of the variation among the cultivars in 7 factors in **Figure 1a**. Samples from 2015 showed higher total amount of flavan-3-ols, quercetins (primarily as quercetin 3-*O*-rutinoside), kaempferols (kaempferol 3-*O*-rutinoside), isorhamnetins, and coumaric acid derivatives than berries of the year 2014. The PLS model did not show clear correlation between years and anthocyanins or sum content of phenolics.

For simple acids and sugars, 'Ben Tirran' had the highest content of simple acids (53 mg/g in 2014 and 52 mg/g in 2015) among all the cultivars studied. Sugars were abundant in 'Tauriai' but poor in 'Ben Finlay'. In the plot of **Figure 1b**, 64% of the chemical variables of simple acids and sugars explained 65% of the variation among the cultivars in 2 factors. Citric acid, fructose, and glucose correlated strongly with the samples collected in year 2015, which explained the higher content of total simple acids and total sugars, respectively, in this year.

In our previous research, the weather condition in the last-months of growth before harvest showed special importance for blackcurrant fruit development,[10,11] since several main primary (sugars) and secondary (anthocyanins) metabolites start accumulating in the last stage of ripening of blackcurrant.[37] In the present study, exceptionally high temperatures including both maximum day time and minimum night time temperatures were observed from mid-July to mid-August of year 2014, which was the last month before harvesting (**Supplemental Table 4**). Zheng *et al*. reported that the average temperature of July correlated positively with the content of citric acid, fructose, and glucose in the Finnish cultivars 'Mortti' and 'Ola', based on analysis of berry samples collected in multiple years.[38] In our study, temperatures were higher than those in the study of Zheng *et al*.[38], and our results showed the opposite: higher temperatures were related to the reduction of these sugars

and citric acid. The phenomenon is commonly seen in other species too. It was shown, for instance, in strawberry (*Fragaria ananassa*) fruit that sugar content was negatively correlated to the temperature during fruit development,[39] and high temperatures have been shown to reduce the organic acids in berries of grapevine (*Vitis vinifera*).[40] Yet, our study was not able to determine that the climatic factors resulted in the yearly deviation of chemical composition of blackcurrant berries, due to the data limited to two growing years only.

Comparison of blackcurrant cultivars originating from different countries. PLS models were applied to investigate the difference among the samples in order to establish correlation between individual compounds and the cultivars. The PLS plots in **Figure 2a** show the interactions between chemical compounds and all cultivars of blackcurrants as 74% of the chemical variables explained 65% of the variation among the cultivars in 7 factors. Sum of phenolics and total anthocyanins correlated negatively with the green cultivars ('Venny' and 'Vilma') along the PC1. Along with the expected color-related compounds, myricetins, primarily 3-*O*-glucoside, 3-*O*-arabinoside, and the free aglycone of myricetin, also represented a negative correlation with the green cultivars. Since there was only one Latvian and one Polish cultivar, comparison was conducted among black-fruited cultivars of Scottish, Lithuanian, and Finnish origins.

The Scottish cultivars generally had higher total content of phenolic acid derivatives than the Lithuanian samples **(Figure 2b**; 69% of the chemical variables explained 96% of the variation among the cultivars in 6 factors). Scottish cultivars correlated strongly to the derivatives of both coumaric acid (CoA) and ferulic acid (FeA), primarily as 4-*O*-coumaroylglucose (4-Co-Glu), (*E*&*Z*)-coumaroyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile (Co-meGlu-B1&2), and 1-*O*-feruloylglucose (1-Fe-Glu). Positive correlations of Scottish cultivars were also found with galloylcatechin (GCat) and catechin (Cat). The

315 conjugates of both caffeic acid (CaA) and coumaric acid, peonidin glycosides, flavan-3-ols
316 and ascorbic acid (AsA) were the main variables to separate the Scottish from the Finnish
317 cultivars on the first two PCs in **Figure 2c** (72% variation in X-data explained 96% of the
318 variation Y-data with 6 factors). Compared to the Finnish samples, the Lithuanian cultivars
319 were richer in ascorbic acid and caffeic acid derivatives, mainly as 5-*O*-caffeoylquinic acid
320 (5-CaQA) (**Figure 2d**; 66% of variation in X-data explained 97% of variation in Y-data with
321 5 factors). Also, higher amounts of 3-*O*-coumaroylquinic acid (3-CoQA), and peonidin 3-*O*-
322 glucoside (Po-Glu) characterized the Lithuanian cultivars.
323
324 **Comparison among cultivars within Scottish origin.** The nine Scottish cultivars were
325 classified into three groups as shown in the scores plot of **Figure 3a** based on the variation in
326 the chemical variables (87% of the chemical variables explained 70% of the variation in Y-
327 data with 7 factors). Group A contained cultivars 'Ben Dorain', 'Ben Gairn', 'Ben Starav'
328 and 'Ben Finlay'. Two newly bred cultivars, 'S 18/2/23' and '9154-3', belonged to group B;
329 group C consisted of 'Ben Hope', 'Ben Tirran', and 'Ben Tron'. Since a single PLS model
330 was not able to differentiate all Scottish blackcurrants, the comparison was performed by
331 groups.
332 In **Figure 3b**, 76% of the chemical variables explained 98% of the variation among the
333 cultivars in 5 factors, and the cultivars in group A had higher amounts of sum-content of
334 phenolic and total anthocyanins than group B. Positive correlations of group A were found
335 with cyanidin 3-*O*-rutinoside (Cy-Rut), petunidin 3-*O*-glucoside (Pt-Glu), pelargonidin 3-*O*-
336 glucoside (Pl-Glu), and all glycosides of delphinidin (De) identified. Group B correlated
337 mainly to 4-*O*-caffeoylglucose (4-Ca-Glu) and 4-Co-Glu. The blackcurrants in group C
338 contained more phenolic acid derivatives (CaA and FeA) and flavan-3-ols than those in
339 Group A (**Figure 3c**; 54% of the chemical variables explained 98% of the variation among

the cultivars with 3 factors). Many of the minor flavonols, myricetin 3-*O*-galactoside (My-Gal), quercetin 3-*O*-galactoside (Qu-Gal), quercetin 3-*O*-arabinoside (Qu-Ara) and isorhamnetin 3-*O*-(6"-malonyl)-galactoside (Is-maGal) were not observed in the group C, which also distinguished these cultivars from others (**Figure 3c**, **Supplemental Table 5**). **Figure 3d** (84% of the variation in X-data explained 99% of the variation in Y-data with 5 factors) indicated that group B was low in sum content of all studied phenolics compared to group C, which was mostly due to the low content of anthocyanins (including De, Cy, Pt, Pl, and Po compounds) and flavonols (myricetin derivatives).

The variations within the groups A-C of Scottish cultivars observed in **Figure 3** were further examined in PLS regression plots in **Figure 4**. 'Ben Dorain' correlated strongly to citric acid (CiA), fructose (Fru), glucose (Glu), total simple organic acids, and total sugars (**Figure 4a**; 91% of the chemical variables explained 99% of the variation among the cultivars in 6 factors). 'Ben Starav' correlated positively to both sucrose (Suc) and quinic acid (QuA) in the plot consisting of factor 2 and factor 4 (not present in this paper). Cyanidin 3-*O*-arabinoside (Cy-Ara) was not found only in 'Ben Gairn'; however, petunidin 3-*O*-rutinoside (Pt-Rut), epicatechin (ECat), and 4-Co-Glu were present at higher contents. 'Ben Finlay' correlated only to (*E*)-feruloyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile (Fe-meGlu-B). For minor components, myricetin 3-*O*-rutinoside (My-Rut), and 3-*O*-coumaroylquinic acid (3-CoQA) showed negative correlations with 'Ben Gairn', but 1-*O*-coumaroylglucose (1-Co-Glu) correlated positively to 'Ben Gairn'.

The common difference between two cultivars in group B was that 'S18/2/23' was more abundant in citric acid, ascorbic acid, and sucrose, whereas the cultivar of '9154-3' strongly correlated to the total content of flavonols, owing to the high concentration of glycosides of quercetin (Qu), and kaempferol (Ka) **(Figure 4b**; 67% of the variation in X-data explained 99% of the variation in Y-data with 2 factors). Phenolic acids in 'S18/2/23' were mainly

present as the derivatives of caffeic acid, but more ferulic acid conjugates were found in '9154-3'.

Figure 4c showed 96% of the chemical variables explained 100% of the variation among the cultivars in group C with 5 factors. 'Ben Tirran' contained the highest amount of citric acid and ascorbic acid. 'Ben Tron' exhibited positive correlations with most of the glycosides of anthocyanidins, which explained the highest sum-content of phenolics among the samples in group C. Yet, delphinidin 3-*O*-(6"-coumaroyl)-glucoside (De-coGlu) and cyanidin 3-*O*-(6"-coumaroyl)-glucoside (Cy-coGlu) were abundant in 'Ben Tirran'. 'Ben Tirran' was also rich in galloylcatechin (GCat), myricetin aglycone (My agly), and ferulic acid derivatives. High concentration of total flavonols and caffeic acid derivatives correlated positively to 'Ben Tron', mainly due to the presence of Qu-Glu, 5-CaQA, and Ka-Gal. Moreover, 3-*O*-coumaroylquinic acids (3-CoQA), quercetin 3-*O*-(6"-malonyl)-glucoside (Qu-maGlu) and a coumaroylquinic acid isomer (CoQA) were quantified mostly in 'Ben Hope'.

Comparison of Finnish cultivars. Aside from anthocyanins, the Finnish green cultivars 'Venny' and 'Vilma' contained high amounts of ascorbic acid, kaempferol glycosides (Ka-Gal and Ka-Rut), and the derivatives of phenolic acids (4-Co-Glu, 1-Co-Glu, Co-meGlu-B2, and 1-Ca-Glu) compared to black ones. Additionally, myricetin was concentrated in black cultivars in form of both glycosides (3-*O*-glucoside, 3-*O*-rutinoside, deoxylhexoside, and 3-*O*-arabinoside) and aglycone (**Figure 5a**). The PLS model in **Figure 5b** presents the variation (90% in X-data) among Finnish black cultivars (99% in Y-data with 4 factors). The sum of all phenolic compounds, including the main glycosides of delphinidin and myricetin, were most abundant in the cultivar 'Marski'. Quercetins correlated strongly with 'Mikael' as 3-*O*-glucoside, 3-*O*-galactoside, and 3-*O*-arabinoside. 'Mortti' contained the highest levels of sucrose and 3-*O*-coumaroylquinic acid but the lowest concentrations of cyanidins, peonidins,

malvidins, and total flavonols. 'Venny' and 'Vilma' shared similar compositional characteristics, which was not surprising, both being offsprings of the cultivar 'Vertti'. 'Vilma' highly correlated with the content of sucrose and (*E*)-feruloyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile (Ca-meGlu-B), whereas 'Venny' correlated mainly with malic acid (MaA), ascorbic acid, quinic acid, quercetin 3-*O*-rutinoside, and galloylcatechin (**Figure 5c**; 92% of the variation explained 98% of the variation among the two green cultivars with 3 factors).

Comparison of Lithuanian cultivars. Lithuanian samples were grouped as displayed in **Supplemental Figure 2a&b**. Group A consisted of 'Almiai', 'Dainiai', and 'Gagatai', presenting higher concentration of anthocyanins (mostly as De, Cy, and Po), myricetin glycosides, and phenolic acids (FeA derivatives) than both 'Joniniai' and 'Tauriai' in group B. Among the samples in group A, 'Almiai' correlated positively to simple organic acids (mainly as CiA); whereas sucrose, malic acid, and quinic acid were abundant in 'Dainiai' (**Supplemental Figure 2c**). The highest level of total anthocyanins was present in 'Gagatai', mainly owing to the high content of delphinidin 3-*O*-rutinoside, delphinidin 3-*O*-(6"-coumaroyl)-glucoside, and cyanidin 3-*O*-(6"-coumaroyl)-glucoside. This was in agreement with the results reported by Rubinskiene and co-workers showing higher content of anthocyanins in 'Gagatai' than in 'Joniniai' and 'Almiai'.[41] In the present study, 'Almiai' correlated negatively to the total content of both cyanidins and myricetins. 'Dainiai' contained more (*E*)-coumaroyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile, myricetin 3-*O*-galactoside, and myricetin 3-*O*-(6"-malonyl)-galactoside. **Supplemental Figure 2d** suggested that 'Joniniai' was richer in malic acid, quinic acid, and sucrose than 'Tauriai'. Positive correlations were found between 'Joniniai' and both 3-*O*-glycoisdes and free aglycones of quercetin and myricetin, as well as some minor phenolics such as epicatechin

and 4-*O*-caffeoylglucose. The total content of coumaric acid derivatives was higher in 'Tauriai' due to the presence of two isomers of coumaroyloxymethylene-glucopyranosyloxy-butenenitrile.

To our best knowledge, the present study is the first one revealing systematic information on compositional variation among blackcurrant cultivars originating from different countries. The overall differentiation among cultivars of different origins was highlighted by the concentrations of different phenolic acid derivatives, even after more than five-year of cultivation in the same geographical location with the same climatic condition. The study also found that the contents of organic acids, sugars and phenolic acid derivatives in blackcurrants correlated strongly with growing year. This may have been caused by different weather conditions during fruit development. The results provide important guidelines for the selection of raw materials in food and beverage processing industry. For example, cultivar 'Dainiai' is rich in sucrose, and high levels of ascorbic acid were found in 'Tisel', 'Joniniai', and 'Ben Tirran'. 'S 18/2/23' and '9154-3' are poor sources of anthocyanins compared to other black-fruited cultivars. The manufacturers can select cultivars accordingly based on the requirements of their products.

In addition, the knowledge of variation in metabolites is essential for breeding new cultivars of blackcurrants. Besides agronomic traits such as yield, fruit size and environmental resistance, the chemical composition in fruits of new cultivars will be probably more emphasized, when more specific information of human health-related effects of different compounds will be available in the future. Our results suggest that the breeding programs have resulted in variation in chemical quality of currants developed in different countries. The cultivars from the same country may share more similarities than those created in different countries. Therefore, it would be possible for plant breeding to improve fruit

quality by introducing new quality characteristics from blackcurrant cultivars originating from different countries.

ASSOCIATED CONTENT

Abbreviations Used

malic acid (**MaA**), citric acid (**CiA**), quinic acid (**QuA**), ascorbic acid (**AsA**), fructose anomers (**Fru**), glucose anomers (**Glu**), sucrose (**Sur**), delphinidin 3-*O*-glucoside (**De-Glu**), delphinidin 3-*O*-rutinoside (**De-Rut**), cyanidin 3-*O*-glucoside (**Cy-Glu**), cyanidin 3-*O*-rutinoside (**Cy-Rut**), petunidin 3-*O*-glucoside (**Pt-Glu**), petunidin 3-*O*-rutinoside (**Pt-Rut**), cyanidin 3-*O*-arabinoside (**Cy-Ara**), pelargonidin 3-*O*-glucoside (**Pl-Glu**), pelargonidin 3-*O*-rutinoside (**Pl-Rut**), peonidin 3-*O*-glucoside (**Po-Glu**), peonidin 3-*O*-rutinoside (**Po-Rut**), malvidin 3-*O*-glucoside (**Ma-Glu**), malvidin 3-*O*-rutinoside (**Ma-Rut**), delphinidin 3-*O*-(6"-coumaroyl)-glucoside (**De-coGlu**), cyanidin 3-*O*-(6"-coumaroyl)-glucoside (**Cy-coGlu**), myricetin 3-*O*-rutinoside (**My-Rut**), myricetin 3-*O*-galactoside (**My-Gal**), myricetin 3-*O*-glucoside (**My-Glu**), myricetin 3-*O*-arabinoside (**My-Ara**), myricetin 3-*O*-(6"-malonyl)-galactoside (**My-maGal**), quercetin 3-*O*-rutinoside (**Qu-Rut**), quercetin 3-*O*-galactoside (**Qu-Gal**), quercetin 3-*O*-glucoside (**Qu-Glu**), quercetin 3-*O*-arabinoside (**Qu-Ara**), quercetin 3-*O*-(6"-malonyl)-glucoside (**Qu-maGlu**), kaempferol 3-*O*-rutinoside (**Ka-Rut**), kaempferol 3-*O*-galactoside (**Ka-Gal**), isorhamnetin 3-*O*-glucoside (**Is-Glu**), myricetin aglycone (**My agly**), kaempferol 3-*O*-(6"-malonyl)-glucoside (**Ka-maGlu**), isorhamnetin 3-*O*-(6"-malonyl)-galactoside (**Is-maGal**), myricetin-hexoside-deoxyhexoside (**My-hex-deox**), isorhamnetin 3-*O*-(6"-malonyl)-glucoside (**Is-maGlu**), quercetin aglycone (**Qu agly**), 5-*O*-caffeoylquinic acid (**5-CaQA**), 4-*O*-caffeoylglucose (**4-Ca-Glu**), 1-*O*-caffeoylglucose (**1-Ca-Glu**), coumaroylquinic acid isomer (**CoQA**), 3-*O*-coumaroylquinic acid (**3-CoQA**), 4-*O*-

coumaroylglucose (**4-Co-Glu**), 1-*O*-coumaroylglucose (**1-Co-Glu**), 3-*O*-caffeoylquinic acid (**3-CaQA**), feruloylglucose isomer (**Fe-Glu**), 1-*O*-feruloylglucose (**1-Fe-Glu**), (E)-caffeoyloxymethylene-glucopyranosyloxy-(Z)-butenenitrile (**Ca-meGlu-B**), (E)-coumaroyloxymethylene-glucopyranosyloxy-(Z)-butenenitrile (**Co-meGlu-B1**), (Z)-coumaroyloxymethylene-glucopyranosyloxy-(Z)-butenenitrile (**Co-meGlu-B2**), (E)-feruloyloxymethylene-glucopyranosyloxy-(Z)-butenenitrile (**Fe-meGlu-B**), galloylcatechin (**GCat**), epigalloylcatechin (**EGCat**), (+)-catechin (**Cat**), (-)-epicatechin (**ECat**), aureusidin glucoside (**Au-Glu**).

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Supporting Information

The supporting information is provided: (1) Chromatographs of sugars, simple organic acids and phenolic compounds in cultivars of blackcurrant (**Supplemental Figure 1**); (2) The correlation of chemical compounds with Lithuanian cultivars of blackcurrants (**Supplemental Figure 2**); (3) Information of blackcurrant cultivars studied (**Supplemental Table 1**); (4) Concentrations of the main groups of phenolic compounds in blackcurrants (**Supplemental Table 2**); (5) Concentrations of simple organic acids and sugars in blackcurrants (**Supplemental Table 3**); (6) Climatic factors recorded at the growth location of blackcurrant cultivars from 20th July to 20th August of year 2014 and 2015 (**Supplemental Table 4**); (7) Concentrations of individual compounds identified in blackcurrant cultivars

(**Supplemental Table 5** as an Excel file attached); (8) Information of external standards used in quantification of phenolic compounds (**Supplemental Table 6**).

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Author Contributions

B. Yang, O. Laaksonen, K. Linderborg, S. Karhu and Y. Tian designed the study.

Y. Tian – Identification of compounds using UPLC-DAD-ESI-MS, statistical analysis, and manuscript writing;

O. Laaksonen – Identification of compounds using UPLC-DAD-ESI-MS, statistical analysis, and manuscript writing and revising;

H. Haikonen – Analysis of anthocyanins using HPLC-DAD under Y. Tian and O. Laaksonen supervising;

A.Vanag – Analysis of simple acids and sugars using GC-FID under Y. Tian and O. Laaksonen supervising;

H. Ejaz – Analysis of flavonol glycosides using HPLC-DAD under Y. Tian and O. Laaksonen supervising;

K. Linderborg, S. Karhu, & B. Yang contributed equally to manuscript writing and revising.

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Conflict of Interest

The authors in this manuscript have no conflict of interest.

REFERENCES

1. Vijayan, K.; Chakraborti, S. P.; Ercisli, S.; Ghosh, P. D. NaCI induced morpho-biochemical and anatomical changes in mulberry (*Morus* spp.). *Plant Growth Regul*. **2008**, 56 (1), 61–69.

2. Serce, S.; Ercisli, S.; Sengul, M., Gunduz, K., Orhan, E. Antioxidant activities and fatty acid composition of wild grown myrtle (*Myrtus communis* L.) fruits. *Pharmacogn Mag*. **2010**, *6*, 9–12.

3. Tian, J., Chen, J., Ye, X., Chen, S. Health benefits of the potato affected by domestic cooking: A review. *Food Chem*. **2016**, 202, 165–175.

4. Sandell, M.; Laaksonen, O.; Järvinen, R.; Rostiala, N.; Pohjanheimo, T.; Tiitinen, K.; Kallio, H. Orosensory profiles and chemical composition of black currant (*Ribes nigrum*) juice and fractions of press residue. *J. Agric. Food Chem.* **2009**, *57*, 3718–3728.

5. Gopalan, A.; Reuben, S. C.; Ahmed, S.; Darvesh, A. S.; Hohmann, J.; Bishayee, A. The health benefits of blackcurrants. *Food Funct.* **2012**, *3*(8), 795–809.

6. Laaksonen, O.; Mäkilä, L.; Tahvonen, R.; Kallio, H.; Yang, B. Sensory quality and compositional characteristics of blackcurrant juices produced by different processes. *Food Chem.* **2013**, *138*, 2421–2429.

7. Laaksonen, O.; Mäkilä, L.; Sandell, M.; Salminen, J.; Liu, P.; Kallio, H.; Yang, B. Chemical-sensory characteristics and consumer responses of blackcurrant juices produced by

539 different industrial processes. *Food Bioprocess Tech.* **2014**, *7*, 2877−2888.
540 8. Battino, M.; Beekwilder, J.; Denoyes-Rothan, B.; Laimer, M.; McDougall, G. J.; Mezzetti,
541 B. Bioactive compounds in berries relevant to human health. *Nutr Rev.* **2009**, *67*, S145–150.
542 9. Puupponen-Pimiä, R.; Nohynek, L.; Alakomi, H.-L.; Oksman-Caldentey, K.-M. Bioactive
543 berry compounds – novel tools against human pathogens. *Appl Microbiol Biotechnol.* **2005**,
544 *67*, 8–18.
545 10. Yang, B.; Zheng, J.; Laaksonen, O.; Tahvonen, R.; Kallio, H. Effects of latitude and
546 weather conditions on phenolic compounds in currant (*Ribes* spp.) cultivars. *J. Agric. Food*
547 *Chem.* **2013**, *61*(14), 3517–3532.
548 11. Zheng, J.; Yang, B.; Ruusunen, V.; Laaksonen, O.; Tahvonen, R.; Hellsten, J.; Kallio, H.
549 Compositional differences of phenolic compounds between black currant (*Ribes nigrum* L.)
550 cultivars and their response to latitude and weather conditions. *J. Agric. Food Chem.* **2012**,
551 *60*(26), 6581−6593.
552 12. Zheng, J.; Kallio, H.; Yang, B. Effects of latitude and weather conditions on sugars, fruit
553 acids and ascorbic acid in currant (*Ribes* sp.) cultivars. *J. Sci. Food Agric.* **2009**, *89*, 2011–
554 2023.
555 13. Vagiri, M.; Ekholm, A.; Öberg, E.; Johansson, E.; Andersson, S. C.; Rumpunen, K.
556 Phenols and ascorbic acid in black currants (*Ribes nigrum* L.): variation due to genotype,
557 location, and year. *J. Agric. Food Chem.* **2013**, *61*(39), 9298−9306.
558 14. Mikulic-Petkovsek, M.; Rescic, J.; Schmitzer, V.; Stampar, F.; Slatnar, A.; Koron, D.;
559 Veberic, R. Changes in fruit quality parameters of four *Ribes* species during ripening. *Food*
560 *Chem.* **2015**, *173*, 363–374.
561 15. Milivojevic, J.; Slatnar, A.; Mikulic-Petkovsek, M.; Stampar, F.; Nikolic, M.; Veberic, R.
562 The influence of early yield on the accumulation of major taste and health-related compounds
563 in black and red currant cultivars (*Ribes* spp.). *J. Agric. Food Chem.* **2012**, *60*(10), 2682–

564 2691.
565 16. Pluta, S.; Mądry, W.; Sieczko, L. Phenotypic diversity for agronomic traits in a collection
566 of blackcurrant (*Ribes nigrum* L.) cultivars evaluated in Poland. *Sci Hort*. **2012**, *145*, 136–
567 144.
568 17. Brennan, R. M. Currants and gooseberries. Temperate Fruit Crop Breeding: Germplasm
569 to Genomics, (ed. by J. F. Hancock), *Springer*: The Netherlands, 2008; 177–196.
570 18. Matala, V. Herukan viljely. Puutarhaliiton julkaisuja nro 306. Helsinki, Puutarhaliitto,
571 1999, 267 p.
572 19. Mäkilä, L.; Laaksonen, O.; Alanne, A. L.; Kortesniemi, M.; Kallio, H.; Yang, B. Stability
573 of hydroxycinnamic acid derivatives, flavonol glycosides, and anthocyanins in black currant
574 juice. *J. Agric. Food Chem.* **2016**, *64* (22), 4584–4598.
575 20. Tian, Y.; Liimatainen, J.; Alanne, A. L.; Lindstedt, A.; Liu, P.; Sinkkonen, J.; Kallio, H.;
576 Yang, B. Phenolic compounds extracted by acidic aqueous ethanol from berries and leaves of
577 different berry plants. *Food Chem.* **2017**, *220*, 266–281.
578 21. Gavrilova, V.; Kajdzanoska, M.; Gjamovski, V.; Stefova, M. Separation, characterization
579 and quantification of phenolic compounds in blueberries and red and black currants by
580 HPLC-DAD-ESI-MS^n. *J. Agric. Food Chem.* **2011**, *59*, 4009–4018.
581 22. Wu, X.; Gu, L.; Prior, R. L.; McKay, S. Characterization of anthocyanins and
582 proanthocyanidins in some cultivars of *Ribes*, *Aronia*, and *Sambucus* and their antioxidant
583 capacity. *J. Agric. Food Chem.* **2004**, *52*(26), 7846–7856.
584 23. Ancillotti, C.; Ciofi, L.; Rossini, D.; Chiuminatto, U.; Stahl-Zeng, J.; Orlandini, S.;
585 Furlanetto, S.; Del Bubba, M. Liquid chromatographic/electrospray ionization
586 quadrupole/time of flight tandem mass spectrometric study of polyphenolic composition of
587 different *Vaccinium* berry species and their comparative evaluation. *Anal Bioanal Chem.*
588 **2017**, *409*, 1347–1368.

589 24. Koponen, J. M.; Happonen, A. M.; Auriola, S.; Kontkanen, H.; Buchert, J.; Poutanen, K.
590 S.; Törrönen, A. R. Characterization and fate of black currant and bilberry flavonols in
591 enzyme-aided processing. *J. Agric. Food Chem.* **2008**, *56*, 3136−3144.
592 25. Borges, G.; Degeneve, A.; Mullen, W.; Crozier, A. Identification of flavonoid and
593 phenolic antioxidants in black currants, blueberries, raspberries, redcurrants, and cranberries.
594 *Eur Food Res Technol.* **2010**, *219*, 620–629.
595 26. Määttä, K. R.; Kamal-Eldin, A.; Törrönen, A. R. High-performance liquid
596 chromatography (HPLC) analysis of phenolic compounds in berries with diode array and
597 electrospray ionization mass spectrometric (MS) detection: *Ribes* species. *J. Agric. Food*
598 *Chem.* **2003**, *51*, 6736–6744.
599 27. Anttonen, M. J.; Karjalainen, R. O. High-performance liquid chromatography analysis of
600 black currant (*Ribes nigrum* L.) fruit phenolics grown either conventionally or organically. *J.*
601 *Agric. Food Chem.* **2006**, *54*, 7530–7538.
602 28. Lu, Y.; Foo, L. Y.; Wong, H. Nigrumin-5-*p*-coumarate and nigrumin-5-ferulate, two
603 unusual nitrile-containing metabolites from black currant (*Ribes nigrum*) seed.
604 *Phytochemistry* **2002**, *59*, 465−468.
605 29. Cyboran, S.; Bonarska-Kujawa, D.; Pruchnik, H.; Żyłka, R.; Oszmiański, J.;
606 Kleszczyńska, H. Phenolic content and biological activity of extracts of blackcurrant fruit and
607 leaves. *Food Res Int*. **2014**, *65*, 47−58.
608 30. Mikulic-Petkovsek, M.; Slatnar, A.; Schmitzer, V.; Stampar, F.; Veberic, R.; Koron, D.
609 Chemical profile of black currant fruit modified by different degree of infection with black
610 currant leaf spot. *Sci. Hortic.* **2013**, *150*, 399–409.
611 31. Määttä-Riihinen, K. R.; Kamal-Eldin, A.; Mattila, P. H.; González-Paramás, A. M.;
612 Törrönen, A. R. Distribution and contents of phenolic compounds in eighteen Scandinavian
613 berry species. *J. Agric. Food Chem.* **2004**, *52*(14), 4477–4486.

614 32. Mattila, P. H.; Hellström, J.; Karhu, S.; Pihlava, J-M.; Veteläinen, M. High variability in
615 flavonoid contents and composition between different North-European currant (*Ribes* spp.)
616 varieties. *Food Chem.* **2016**, *204*, 14–20.
617 33. Nour, V.; Stampar, F.; Veberic, R.; Jakopic, J. Anthocyanins profile, total phenolics and
618 antioxidant activity of black currant ethanolic extracts as influenced by genotype and ethanol
619 concentration. *Food Chem.* **2013**, *141*, 961–966.
620 34. Mikkonen, T.; Määttä, K.; Hukkanen, A.; Kokko, H.; Törrönen, A.; Kärenlampi, S.;
621 Karjalainen, R. Flavonol content varies among black currant cultivars. *J. Agric. Food Chem.*
622 **2001**, *49*, 3274–3277.
623 35. Bordonaba, J. G.; Terry, L. A. Biochemical profiling and chemometric analysis of
624 seventeen UK-grown black currant cultivars. *J. Agric. Food Chem.* **2008**, *56*(16), 7422–7430.
625 36. Woznicki, T. L.; Sønsteby, A.; Aaby, K.; Martinsen, B. K.; Heide, O. M.; Wold, A. B.;
626 Remberg, S. F. Ascorbate pool, sugars and organic acids in black currant (*Ribes nigrum* L.)
627 berries are strongly influenced by genotype and post-flowering temperature. *J. Sci. Food*
628 *Agric*. **2017**, *97*(4), 1302–1309.
629 37. Jarret, D. A.; Morris, J.; Cullen, D. W.; Gordon, S. L.; Verrall, S. R.; Milne, L.; Hedley P.
630 E.; Allwood, J. W.; Brennan, R. M.; Hancock, R. D. A transcript and metabolite atlas of
631 blackcurrant fruit development highlights hormonal regulation and reveals the role of key
632 transcription factors. *Front Plant Sci.* **2018**, *9*, 1235.
633 38. Zheng, J.; Yang, B.; Tuomasjukka, S.; Ou, S.; Kallio, H. Effects of latitude and weather
634 conditions on contents of sugars, fruit acids, and ascorbic acid in black currant (*Ribes nigrum*
635 L.) juice. *J. Agric. Food Chem.* **2009**, *57*, 2977–2987.
636 39. MacKenzie, S. J.; Chandler, C. K.; Hasing, T.; Whitaker, V. M. The role of temperature
637 in the late-season decline in soluble solids content of strawberry fruit in a subtropical
638 production system. *HortScience* **2011**, *46*, 1562–1566.

40. Sweetman, C.; Sadras, V. O.; Hancock, R. D.; Soole, K. L.; Ford, C. M. Metabolic effects of elevated temperature on organic acid degradation in ripening *Vitis vinifera* fruit. *J. Exp. Bot.* **2014**, *65*, 5975–5988.

41. Rubinskiene, M.; Viskelis, P.; Jasutiene, I.; Viskeliene, R.; Bobinas, C. Impact of various factors on the composition and stability of black currant anthocyanins. *Food Res Int*. **2005**, *38*, 867–871.

Figure captions

Figure 1. PLS models of comparison of blackcurrant cultivars in two different growing years: a. phenolic compounds (n=8662), b. sugars and simple organic acids (n=1098). Legend of the scores plots: ○ for the samples harvested in Year 2015, □ means the samples harvested in Year 2014. In the loading plots, the growing year is in red bold italic font and the identified phenolic compounds are in blue font. The full names of these compounds are referred in **Table 1**.

Figure 2. PLS models of comparison of blackcurrant cultivars originating from different countries: based on chemical variables (n=X) a. all cultivars (n=9760), b. the black cultivars (n=6560) originating from Scotland and Lithuanian, c. the black cultivars originating (n=5600) from Scotland and Finland, d. the black cultivars (n=3840) originating from Lithuanian and Finland. Legend of the scores plots: ■ for Scottish samples, ● for Lithuanian samples, ▲ for Latvian samples, ◆ for Finnish black-fruited samples, ▼ for Finnish green-fruited samples, and ✳ for Polish samples. In the loading plots, the origin of country is in red bold italic font and the identified phenolic compounds are in blue font. The full names of the compounds are referred in **Table 1.**

664

665 **Figure 3. PLS models of comparison of main groups of Scottish cultivars**: a. all Scottish
666 cultivars (n=4160), b. the comparison between groups A and B (n=2720), c. the comparison
667 between groups A and C (n=3200), d. the comparison between groups B and C (n=2400). In
668 the loading plots, the names of cultivars and groups are in red bold italic font and the
669 identified phenolic compounds are in blue font. The full names of the compounds are referred
670 in **Table 1.**

671

672 **Figure 4. Comparison of Scottish cultivars with PLS regression models based on their**
673 **chemical composition**: a. the comparison within group A (n=2400), b. the comparison within
674 group B (n=960), c. the comparison within group C (n=1140). The groups are based on the
675 model in **Figure 3**. The name of cultivars is in red bold italic font and the identified phenolic
676 compounds are in blue font. The full names of the compounds are referred in **Table 1.**

677

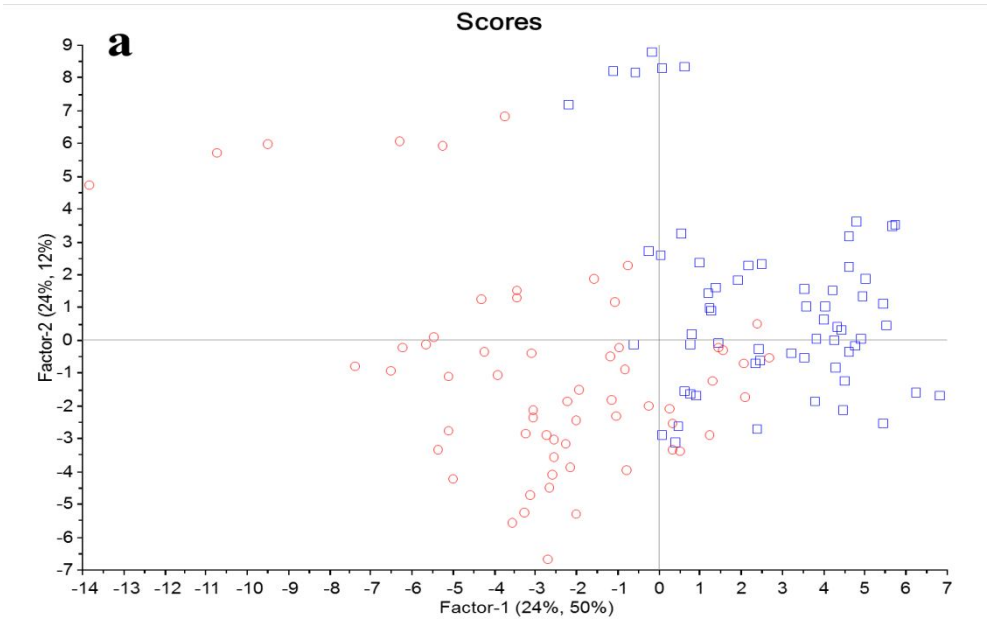
678 **Figure 5. Comparison of Finnish cultivars with PLS regression models based on their**
679 **chemical composition**: a. all Finnish cultivars (n=2400), b. black cultivars (n=1440), c. green
680 cultivars (n=960). In the loading plots, the name of cultivars is in red bold italic font and the
681 identified phenolic compounds are in blue font. The full names of compounds are referred in
682 **Table 1.**

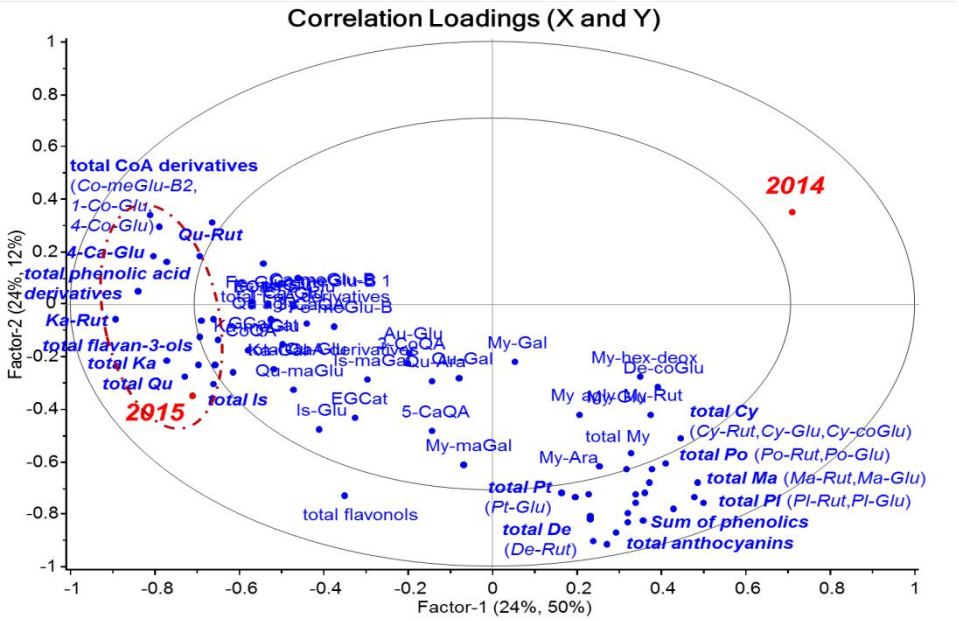
Table 1 Identification of phenolic compounds, organic acids, and sugars in blackcurrant (*Ribes nigrum*) cultivars

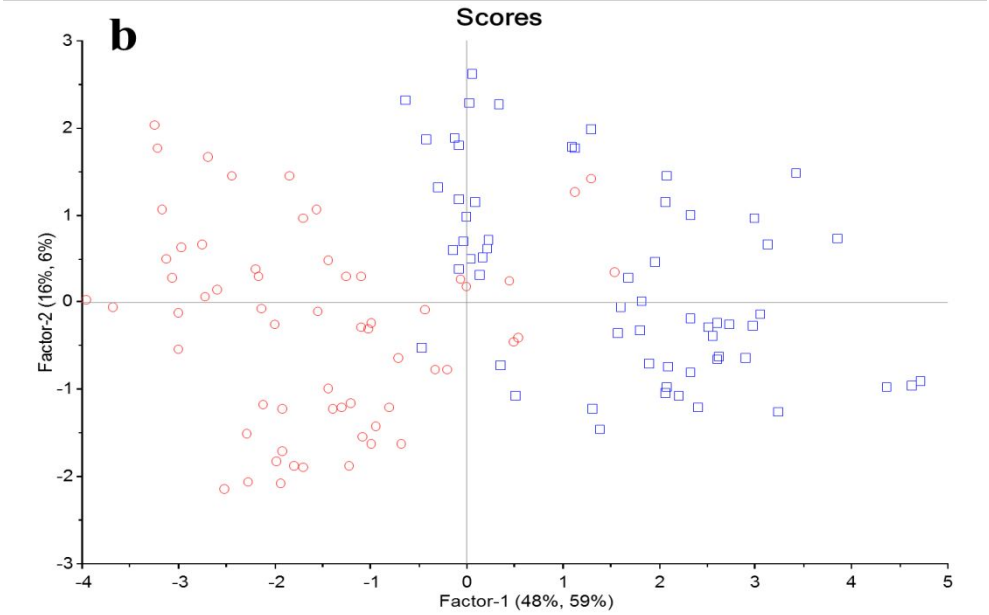
No.[a]	Tentative identification[b]	Abbreviation[c]	UV λ_{max} (*nm*)	$[M-H]^-/[M+H]^+$ (*m/z*)	$[A-H]^-/[A+H]^+$ and other ions (*m/z*)	Identification by
	Anthocyanins					
1	delphinidin 3-*O*-glucoside	De-Glu	276,524	463/-	301/-	MS, Standard & Literature[6,20-23]
2	delphinidin 3-*O*-rutinoside	De-Rut	276,525	609/-	301/-	MS & Literature[6,20-23]
3	cyanidin 3-*O*-glucoside	Cy-Glu	280,516	447/-	285/-	MS, Standard & Literature[6,20-23]
4	cyanidin 3-*O*-rutinoside	Cy-Rut	280,517	593/-	285/-	MS, Standard & Literature[6,20-23]
5	petunidin 3-*O*-glucoside	Pt-Glu	276,527	477/-	315/-	MS & Literature[20-23]
6	petunidin 3-*O*-rutinoside	Pt-Rut	276,527	623/-	315/-	MS & Literature[20-23]
7	cyanidin 3-*O*-arabinoside	Cy-Ara	280,516	417/-	285/-	MS & Literature[20-23]
8	pelargonidin 3-*O*-glucoside	Pl-Glu	278,525	431/-	269/-	MS & Literature[21-23]
9	pelargonidin 3-*O*-rutinoside	Pl-Rut	278,525	577/-	269/-	MS & Literature[21-23]
10	peonidin 3-*O*-glucoside	Po-Glu	280,517	461/-	299/-	MS & Literature[20-23]
11	peonidin 3-*O*-rutinoside	Po-Rut	280,517	607/-	299/-	MS & Literature[20-23]
12	malvidin 3-*O*-glucoside	Ma-Glu	281,522	491/-	329/-	MS & Literature[20-23]
13	malvidin 3-*O*-rutinoside	Ma-Rut	281,522	637/-	329/-	MS & Literature[20-23]
14	delphinidin 3-*O*-(6"-coumaroyl)-glucoside	De-coGlu	280,530	609/-	447,301/-	MS & Literature[20-23]
15	cyanidin 3-*O*-(6"-coumaroyl)-glucoside	Cy-coGlu	280,524	593/-	447,285/-	MS & Literature[20-23]
	Flavonols					
16	myricetin 3-*O*-rutinoside	My-Rut	255,265(sh),355	625/627	317/481,319	MS, Standard & Literature[19,20,24,25]
17	myricetin 3-*O*-galactoside	My-Gal	255,265(sh),355	479/481	317/319	MS, Standard & Literature[19,20,24]
18	myricetin 3-*O*-glucoside	My-Glu	255,265(sh),355	479/481	317/319	MS, Standard & Literature[19,20,24]
19	myricetin 3-*O*-arabinoside	My-Ara	255,265(sh),355	449/451	317/319	MS & Literature[19,20,24,25]
20	myricetin 3-*O*-(6"-malonyl)-galactoside	My-maGal	256,266(sh),356	565/567	521,317/319	MS & Literature[19,20]
21	quercetin 3-*O*-rutinoside	Qu-Rut	255,265(sh),355	609/611	301/465,303	MS, Standard & Literature[19,20,24,25]
22	quercetin 3-*O*-galactoside	Qu-Gal	255,265(sh),355	463/465	301/303	MS, Standard & Literature[19,20,24]
23	quercetin 3-*O*-glucoside	Qu-Glu	255,265(sh),355	463/465	301/303	MS, Standard & Literature[19,20,24,25]
24	quercetin 3-*O*-arabinoside	Qu-Ara	255,266(sh),355	433/435	301/303	MS & Literature[20]
25	quercetin 3-*O*-(6"-malonyl)-glucoside	Qu-maGlu	256,266(sh),356	549/551	505,301/303	MS & Literature[19,20,24,25]
26	kaempferol 3-*O*-rutinoside	Ka-Rut	266,346	593/595	285/449,287	MS & Literature[19,20,24,25]
27	kaempferol 3-*O*-galactoside	Ka-Gal	266,346	447/449	285/287	MS & Literature[20,25]
28	isorhamnetin 3-*O*-glucoside	Is-Glu	256,265(sh),354	477/479	315/317	MS, Standard & Literature[19,20,24]
29	myricetin aglycone	My agly	255,266(sh),370	317/319		MS & Literature[19,20,24]
30	kaempferol 3-*O*-(6"-malonyl)-glucoside	Ka-maGlu	265,465	533/535	489,285/287	MS & Literature[19,20]
31	isorhamnetin 3-*O*-(6"-malonyl)-galactoside	Is-maGal	256,265(sh),355	563/565	519,315/317	MS & Literature[19,20,24]
32	myricetin-hexoside-deoxyhexoside	My-hex-deox	255,268(sh),356	625/627	317/319	MS & Literature[20]
33	isorhamnetin 3-*O*-(6"-malonyl)-glucoside	Is-maGlu	256,265(sh),355	563/565	519,315/317	MS & Literature[19,20]

34	quercetin aglycone	Qu agly	274,368	301/303		MS & Literature[19,20,24]
	Phenolic acid derivatives					
35	5-*O*-caffeoylquinic acid	5-CaQA	295(sh),325	353/355	191,179/377,163	MS, Standard & Literature[19,20,26]
36	4-*O*-caffeoylglucose	4-Ca-Glu	298(sh),328	341/343	179,161/365,163	MS & Literature[19,20,26,27]
37	1-*O*-caffeoylglucose	1-Ca-Glu	296(sh),324	341/343	179,161/365,163	MS & Literature[19,20,26,27]
38	coumaroylquinic acid isomer	CoQA	290(sh),310	337/339	191,163/361,147	MS & Literature[19,20,26]
39	3-*O*-coumaroylquinic acid	3-CoQA	292(sh),314	337/339	191,163/361,147	MS & Literature[19,20,26]
40	4-*O*-coumaroylglucose	4-Co-Glu	298(sh),314	325/327	163/349,165	MS & Literature[19,20,26,27]
41	1-*O*-coumaroylglucose	1-Co-Glu	298(sh),314	325/327	163/349,165	MS & Literature[19,20,26,27]
42	3-*O*-caffeoylquinic acid	3-CaQA	295(sh),325	353/355	191,179/377,163	MS & Literature[19,20,26]
43	feruloylglucose isomer	Fe-Glu	298(sh),318	355/357	193,175/379,177	MS & Literature[19,20,26,27]
44	1-*O*-feruloylglucose	1-Fe-Glu	298(sh),318	355/357	193,175/379,177	MS & Literature[19,20,26,27]
45	(*E*)-caffeoyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile	Ca-meGlu-B	296(sh),329	436/438	179,135/460,276	MS & Literature[19,28]
46	(*E*)-coumaroyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile	Co-meGlu-B1	290(sh),314	420/422	163,119/444,260	MS & Literature[19,28]
47	(*Z*)-coumaroyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile	Co-meGlu-B2	290(sh),314	420/422	163,119/444,260	MS & Literature[19,28]
48	(*E*)-feruloyloxymethylene-glucopyranosyloxy-(*Z*)-butenenitrile	Fe-meGlu-B	290(sh),328	450/452	193,134/474,290	MS & Literature[19,27,28]
	Flavan-3-ols					
49	galloylcatechin	GCat	280	305/307		MS
50	epigalloylcatechin	EGCat	280	305/307		MS
51	(+)-catechin	Cat	280	289/291		MS, Standard & Literature[20,29]
52	(-)-epicatechin	ECat	280	289/291		MS, Standard & Literature[20,29]
	Other phenolics					
53	aureusidin glucoside	Au-Glu	280,325(sh)	447/449	285/287	MS & Literature[19]
	Organic acids					
54	malic acid	MaA	-	-	-	Standard & Literature[12,30]
55	citric acid	CiA	-	-	-	Standard & Literature[12,30]
56	quinic acid	QuA	-	-	-	Standard & Literature[12]
57	ascorbic acid	AsA	-	-	-	Standard & Literature[12,30]
	Sugars					
58-60	fructose anomers	Fru	-	-	-	Standard & Literature[12,30]
61,62	glucose anomers	Glu	-	-	-	Standard & Literature[12,30]
63	sucrose	Sur	-	-	-	Standard & Literature[12,30]

[a] The number of compounds is referred in **Supplemental Figure 1**. [b] Phenolic compounds were identified using UPLC-DAD-ESI-MS with the comparison of reference standards and previous literature. Both organic acids and sugars were identified using GC-FID with internal reference standards. [c] The abbreviation of each compound is used in PLS regression models.


a
Scores
Factor-2 (24%, 12%)
Factor-1 (24%, 50%)


Correlation Loadings (X and Y)
total CoA derivatives
(Co-meGlu-B2,
1-Co-Glu,
4-Co-Glu)
Qu-Rut
4-Ca-Glu
total phenolic acid
derivatives
Ka-Rut
total flavan-3-ols
total Ka
total Qu
2015
total Is
Is-Glu
EGCat
Qu-maGlu
5-CaQA
My-maGal
total flavonols
My-Gal
My-hex-deox
De-coGlu
total My
My-Ara
total Pt
(Pt-Glu)
total De
(De-Rut)
total Cy
(Cy-Rut,Cy-Glu,Cy-coGlu)
total Po (Po-Rut,Po-Glu)
total Ma (Ma-Rut,Ma-Glu)
total Pl (Pl-Rut,Pl-Glu)
Sum of phenolics
total anthocyanins
2014
Factor-2 (24%, 12%)
Factor-1 (24%, 50%)


b
Scores
Factor-2 (16%, 6%)
Factor-1 (48%, 59%)

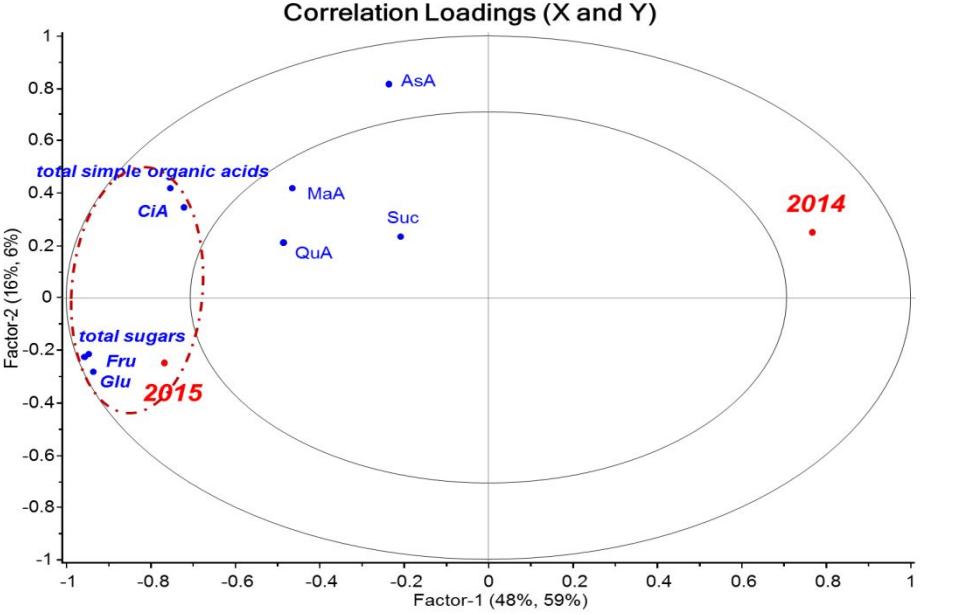
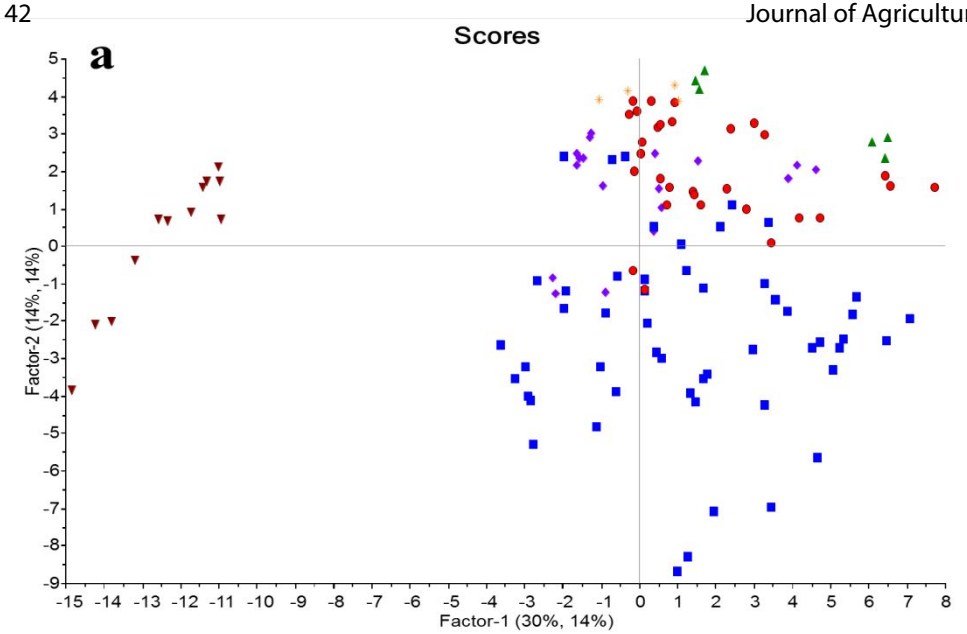
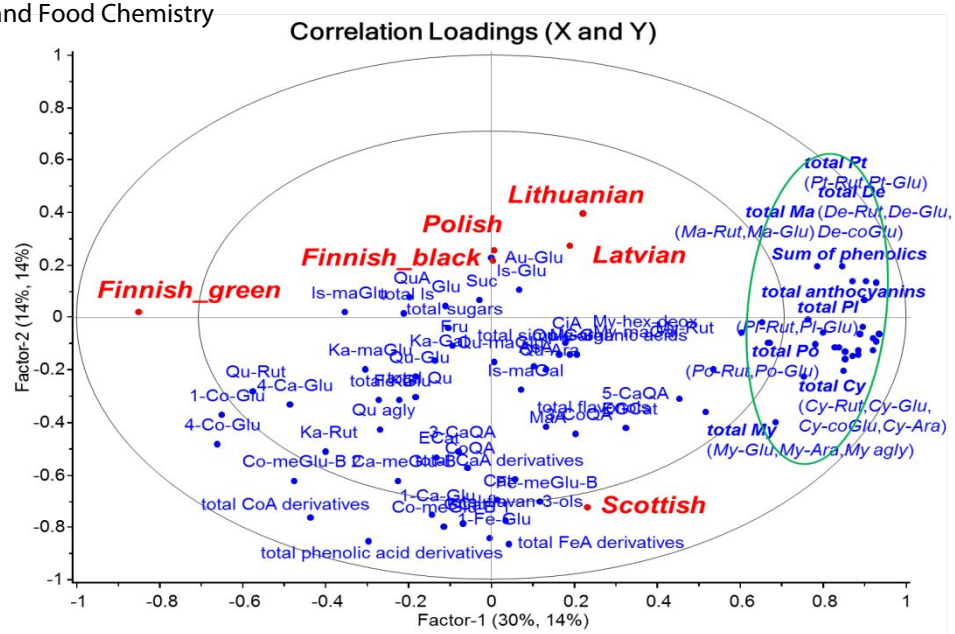
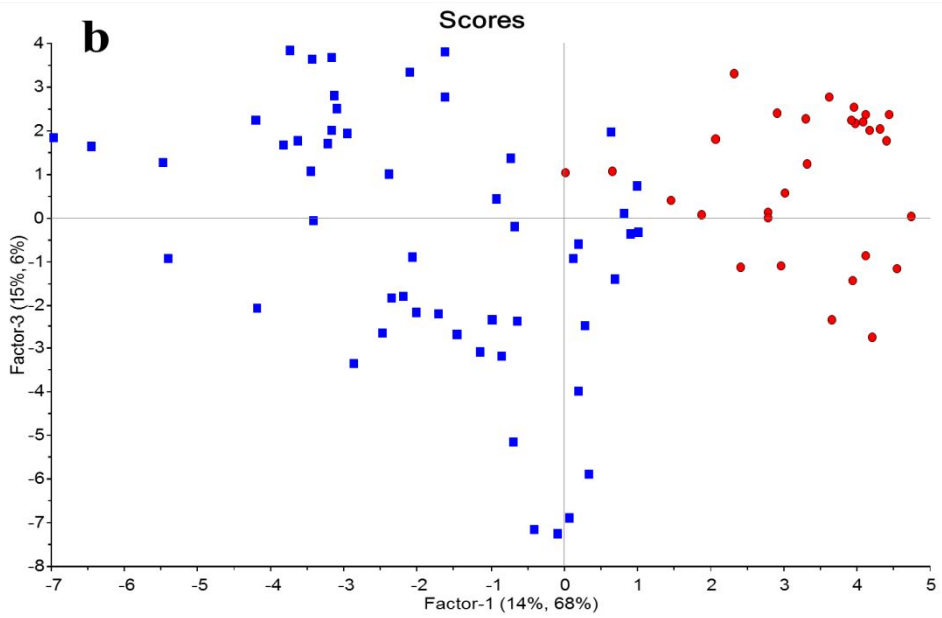
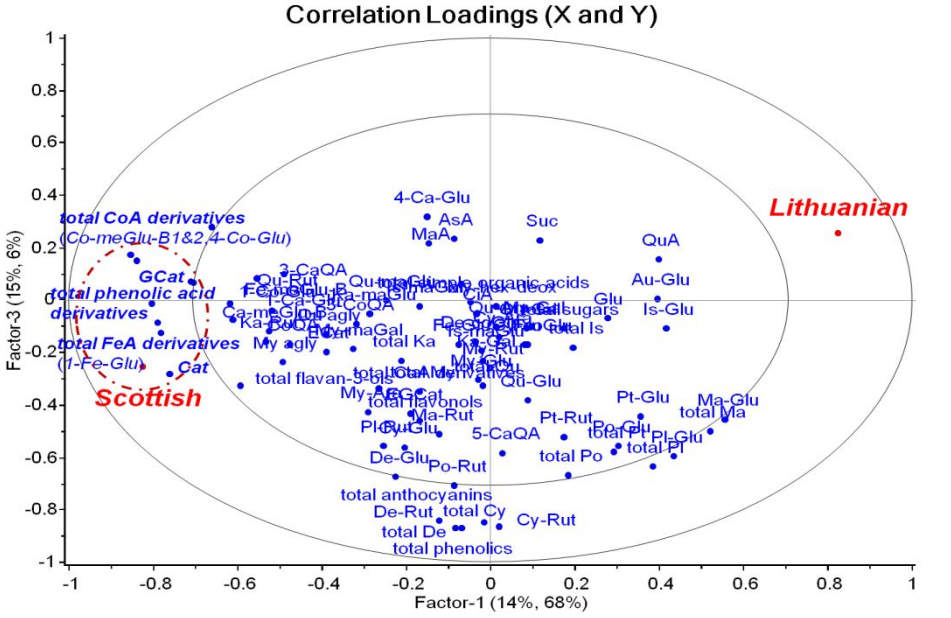

Correlation Loadings (X and Y)
AsA
total simple organic acids
CiA
MaA
Suc
QuA
total sugars
Fru
Glu
2015
2014
Factor-2 (16%, 6%)
Factor-1 (48%, 59%)

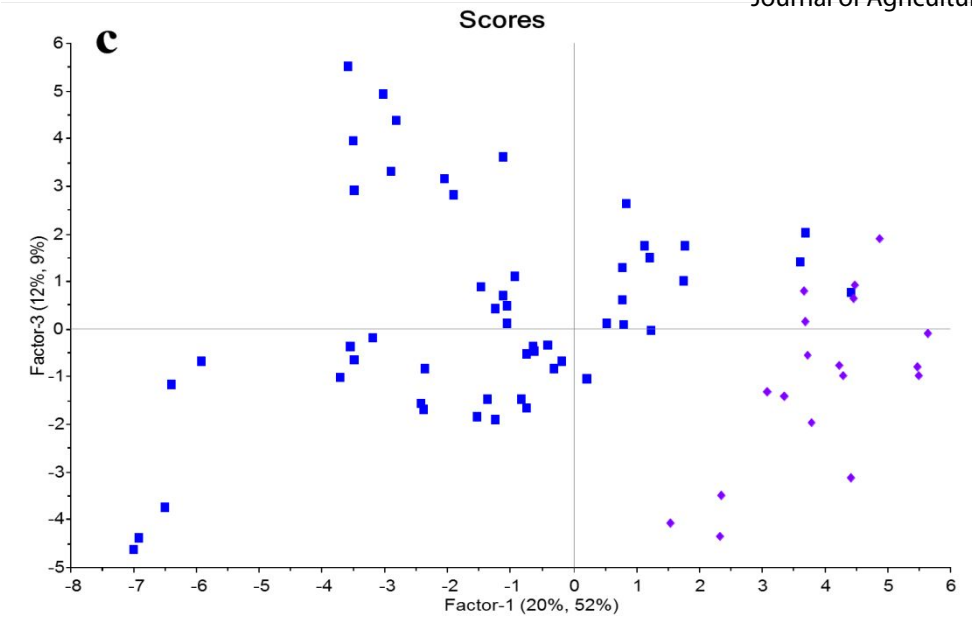
Figure 1

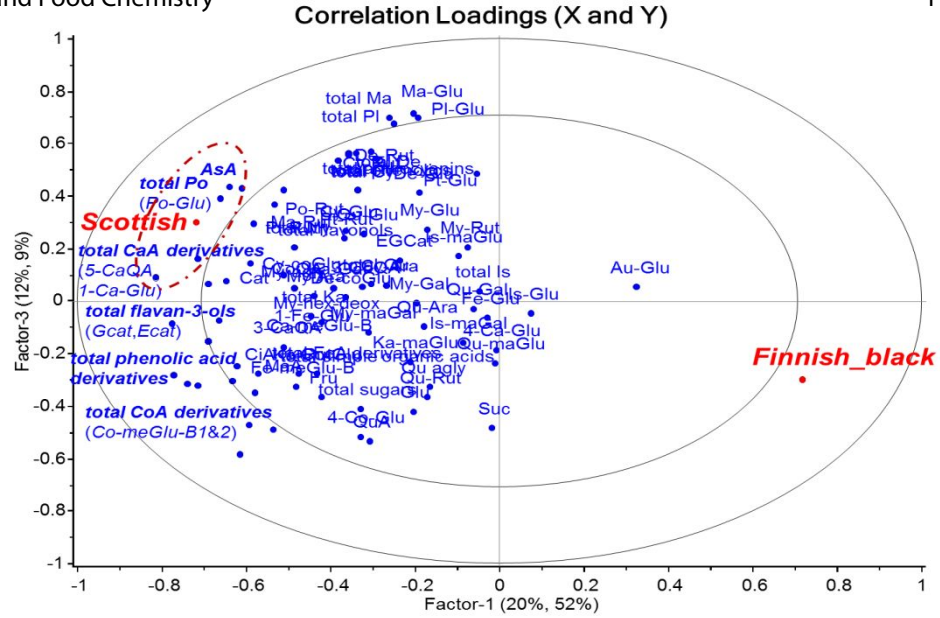

a
Scores
Factor-2 (14%, 14%)
Factor-1 (30%, 14%)

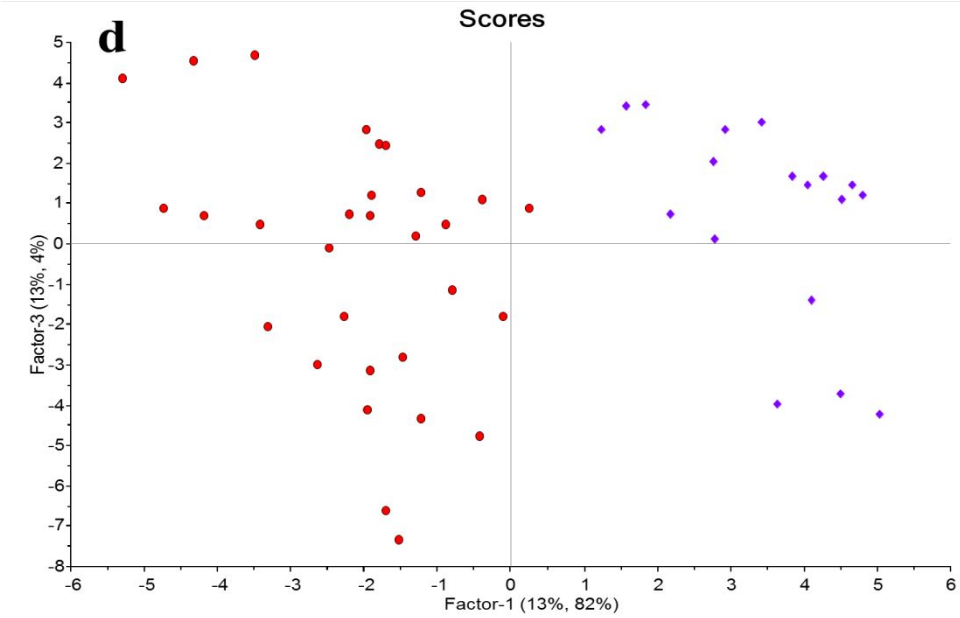

Correlation Loadings (X and Y)
Factor-2 (14%, 14%)
Factor-1 (30%, 14%)
Lithuanian
Polish
Finnish_black
Latvian
Finnish_green
Scottish
total Pt (Pt-Rut,Pt-Glu)
total De
total Ma (De-Rut,De-Glu, (Ma-Rut,Ma-Glu) De-coGlu)
Sum of phenolics
total anthocyanins
total Pl (Pl-Rut,Pl-Glu)
total Po (Po-Rut,Po-Glu)
total Cy (Cy-Rut,Cy-Glu, Cy-coGlu,Cy-Ara)
total My (My-Glu,My-Ara,My agly)
total CoA derivatives
total phenolic acid derivatives
total FeA derivatives


b
Scores
Factor-3 (15%, 6%)
Factor-1 (14%, 68%)


Correlation Loadings (X and Y)
Factor-3 (15%, 6%)
Factor-1 (14%, 68%)
Lithuanian
Scottish
total CoA derivatives (Co-meGlu-B1&2,4-Co-Glu)
total phenolic acid derivatives
GCat
total FeA derivatives (1-Fe-Glu)
Cat


c
Scores
Factor-3 (12%, 9%)
Factor-1 (20%, 52%)


Correlation Loadings (X and Y)
Scottish
AsA
total Po
(Po-Glu)
total CaA derivatives
(5-CaQA,
1-Ca-Glu)
total flavan-3-ols
(Gcat,Ecat)
total phenolic acid
derivatives
total CoA derivatives
(Co-meGlu-B1&2)
Finnish_black
Factor-3 (12%, 9%)
Factor-1 (20%, 52%)


d
Scores
Factor-3 (13%, 4%)
Factor-1 (13%, 82%)

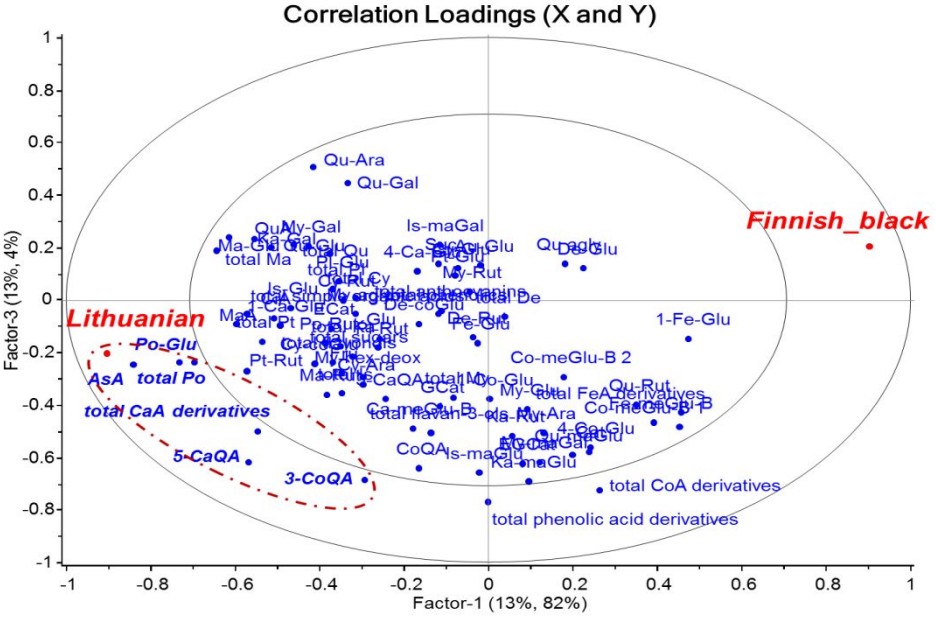
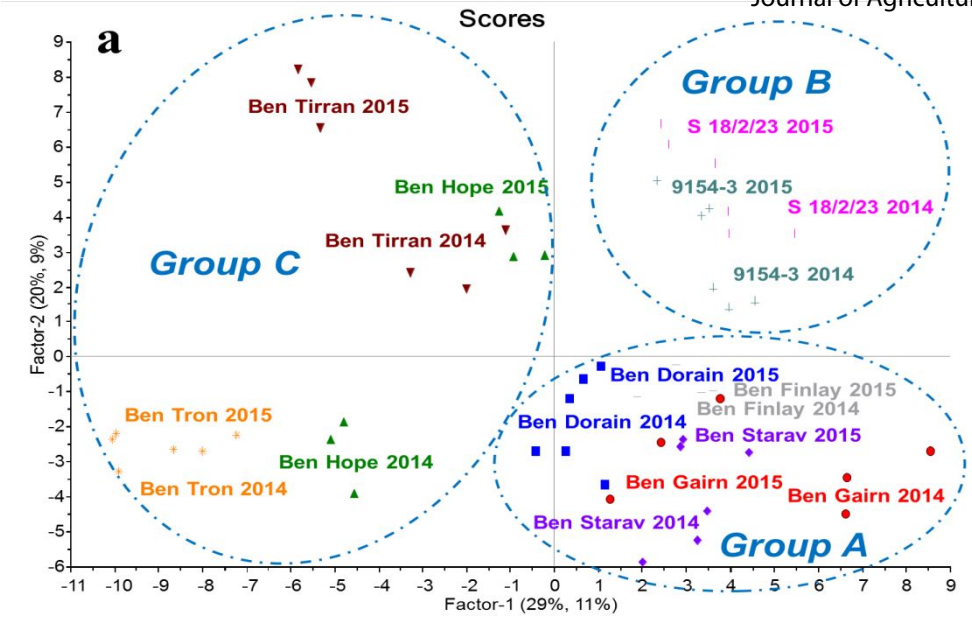
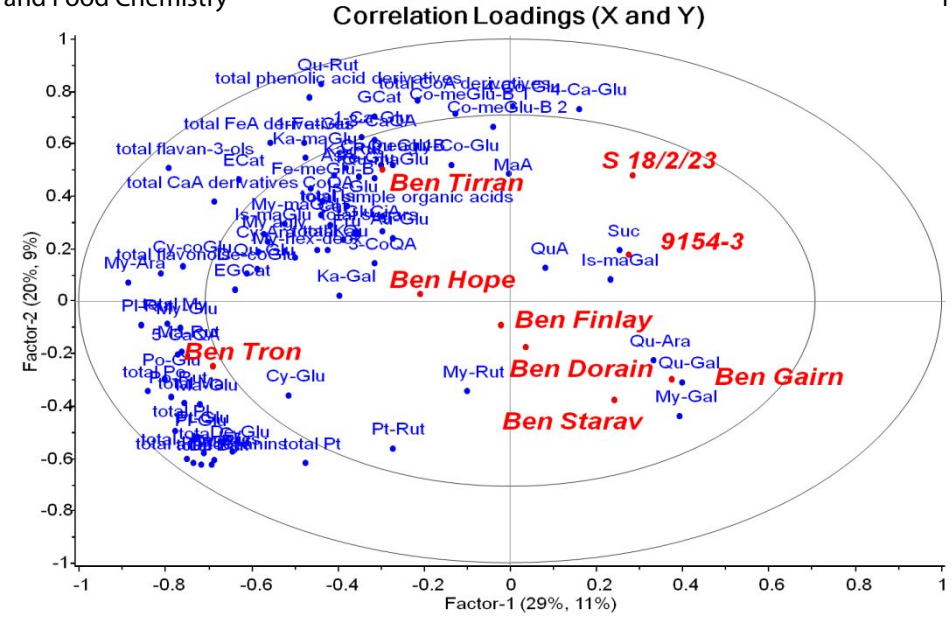
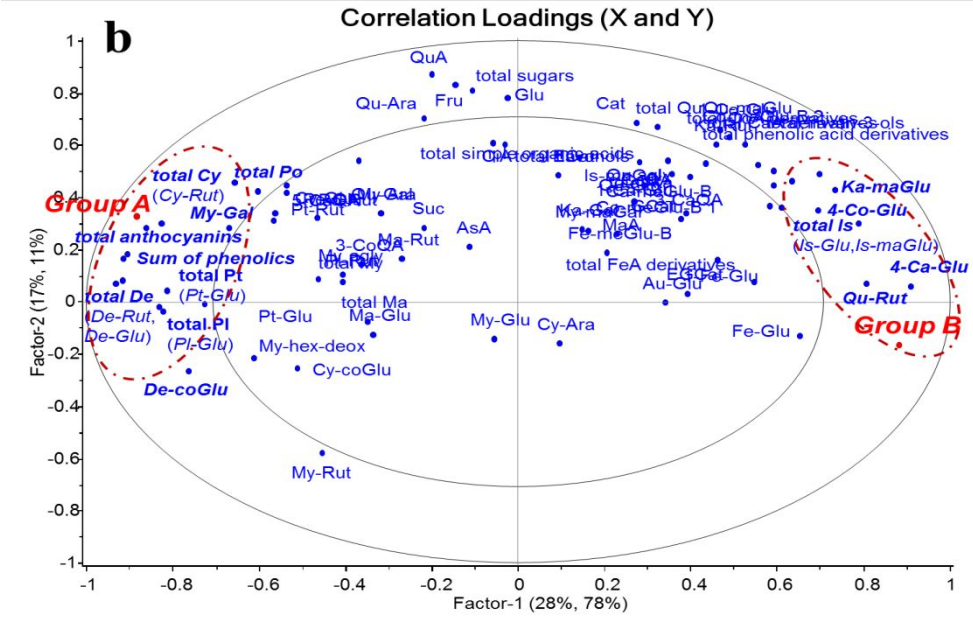
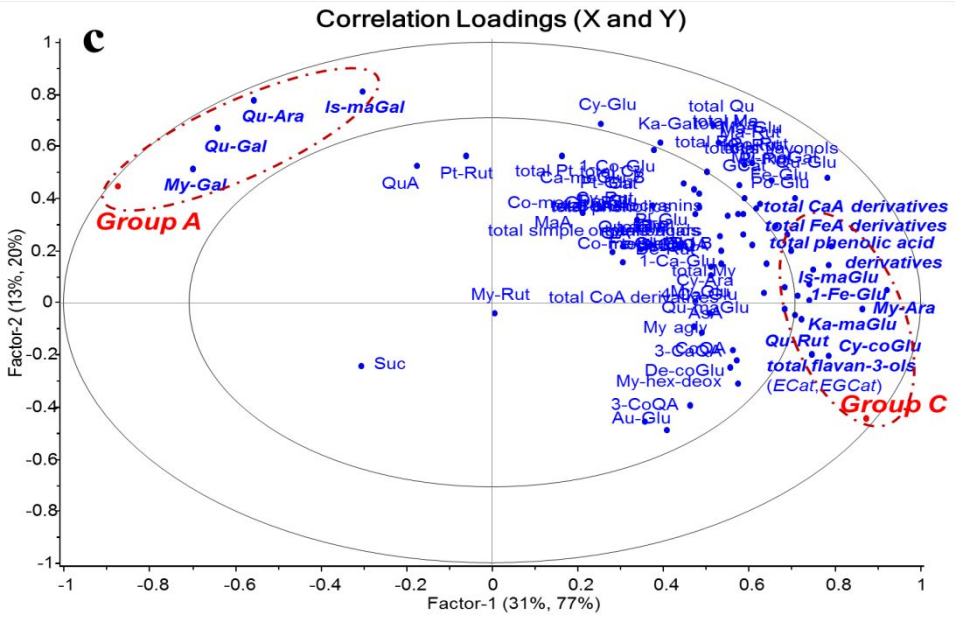

Correlation Loadings (X and Y)
Lithuanian
Po-Glu
AsA
total Po
total CaA derivatives
5-CaQA
3-CoQA
Finnish_black
total CoA derivatives
total phenolic acid derivatives
Factor-3 (13%, 4%)
Factor-1 (13%, 82%)

Figure 2


a
Scores
Group B
Group C
Group A
Ben Tirran 2015
S 18/2/23 2015
Ben Hope 2015
9154-3 2015
S 18/2/23 2014
Ben Tirran 2014
9154-3 2014
Ben Tron 2015
Ben Dorain 2015
Ben Finlay 2015
Ben Finlay 2014
Ben Dorain 2014
Ben Starav 2015
Ben Hope 2014
Ben Gairn 2015
Ben Gairn 2014
Ben Tron 2014
Ben Starav 2014
Factor-2 (20%, 9%)
Factor-1 (29%, 11%)


Correlation Loadings (X and Y)
Ben Tirran
S 18/2/23
9154-3
Ben Hope
Ben Finlay
Ben Tron
Ben Dorain
Ben Gairn
Ben Starav
Factor-2 (20%, 9%)
Factor-1 (29%, 11%)


b
Correlation Loadings (X and Y)
Group A
Group B
Factor-2 (17%, 11%)
Factor-1 (28%, 78%)


c
Correlation Loadings (X and Y)
Group A
Group B
Group C
Factor-2 (13%, 20%)
Factor-1 (31%, 77%)

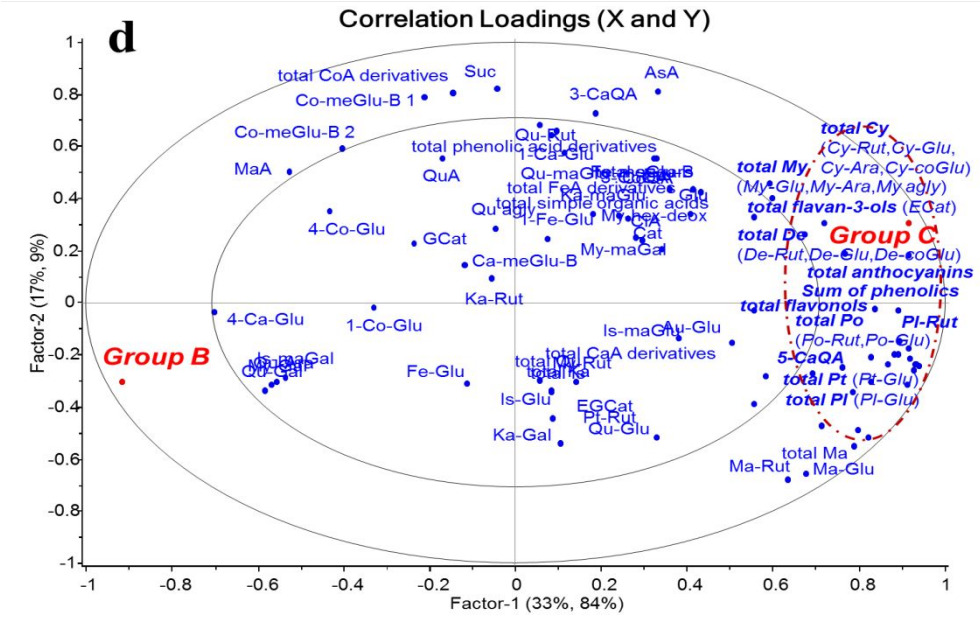
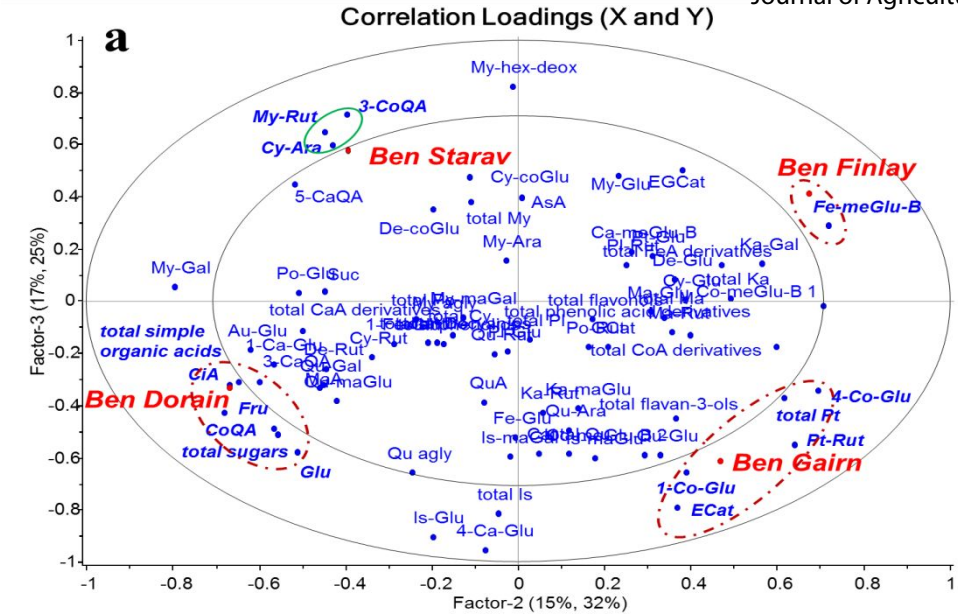
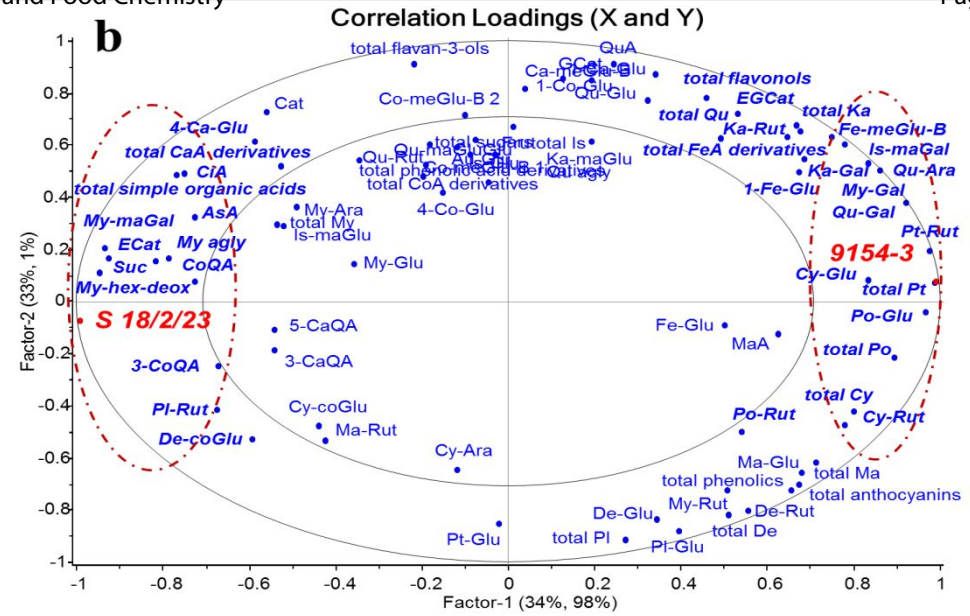

d
Correlation Loadings (X and Y)
Factor-2 (17%, 9%)
Factor-1 (33%, 84%)
total CoA derivatives
Suc
AsA
Co-meGlu-B 1
3-CaQA
Co-meGlu-B 2
Qu-Rut
total phenolic acid derivatives
1-Ca-Glu
MaA
QuA
total FeA derivatives
total simple organic acids
1-Fe-Glu
4-Co-Glu
GCat
Ca-meGlu-B
My-maGal
Ka-Rut
4-Ca-Glu
1-Co-Glu
Is-maGlu
Au-Glu
Group B
total CaA derivatives
Fe-Glu
Is-Glu
EGCat
Pl-Rut
Qu-Glu
Ka-Gal
total Cy
(Cy-Rut,Cy-Glu,
total My
Cy-Ara,Cy-coGlu)
(My-Glu,My-Ara,My agly)
total flavan-3-ols (ECat)
total De
Group C
(De-Rut,De-Glu,De-coGlu)
total anthocyanins
Sum of phenolics
total flavonols
total Po
Pl-Rut
(Po-Rut,Po-Glu)
5-CaQA
total Pt (Pt-Glu)
total Pl (Pl-Glu)
total Ma
Ma-Rut
Ma-Glu

Figure 3


a
Correlation Loadings (X and Y)
Factor-3 (17%, 25%)
Factor-2 (15%, 32%)
Ben Starav
Ben Finlay
Ben Dorain
Ben Gairn
My-hex-deox
My-Rut
3-CoQA
Cy-Ara
Cy-coGlu
My-Glu
EGCat
5-CaQA
AsA
Fe-meGlu-B
De-coGlu
total My
My-Ara
Ka-Gal
My-Gal
Po-Glu
Suc
total CaA derivatives
total phenolic acid derivatives
total Ka
Co-meGlu-B 1
total simple organic acids
Au-Glu
Cy-Rut
1-Ca-Glu
De-Rut
CiA
MaA
Ka-maGlu
QuA
Ka-Rut
Qu-Ara
total flavan-3-ols
4-Co-Glu
Fru
CoQA
Fe-Glu
total Pt
total sugars
Pt-Rut
Glu
Qu agly
total Is
1-Co-Glu
ECat
Is-Glu
4-Ca-Glu


b
Correlation Loadings (X and Y)
Factor-2 (33%, 1%)
Factor-1 (34%, 98%)
9154-3
S 18/2/23
total flavan-3-ols
QuA
total flavonols
EGCat
Cat
Co-meGlu-B 2
total Qu
total Ka
4-Ca-Glu
Ka-Rut
Fe-meGlu-B
total CaA derivatives
total FeA derivatives
Is-maGal
CiA
Ka-Gal
Qu-Ara
total simple organic acids
1-Fe-Glu
My-Gal
My-Ara
4-Co-Glu
Qu-Gal
My-maGal
AsA
total My
Pt-Rut
Is-maGlu
ECat
My agly
My-Glu
Cy-Glu
CoQA
Suc
total Pt
My-hex-deox
Po-Glu
5-CaQA
Fe-Glu
MaA
3-CoQA
3-CaQA
total Po
Cy-coGlu
total Cy
Pl-Rut
Ma-Rut
Po-Rut
Cy-Rut
De-coGlu
Cy-Ara
Ma-Glu
total Ma
total phenolics
total anthocyanins
My-Rut
De-Glu
De-Rut
Pt-Glu
total Pl
total De
Pt-Glu

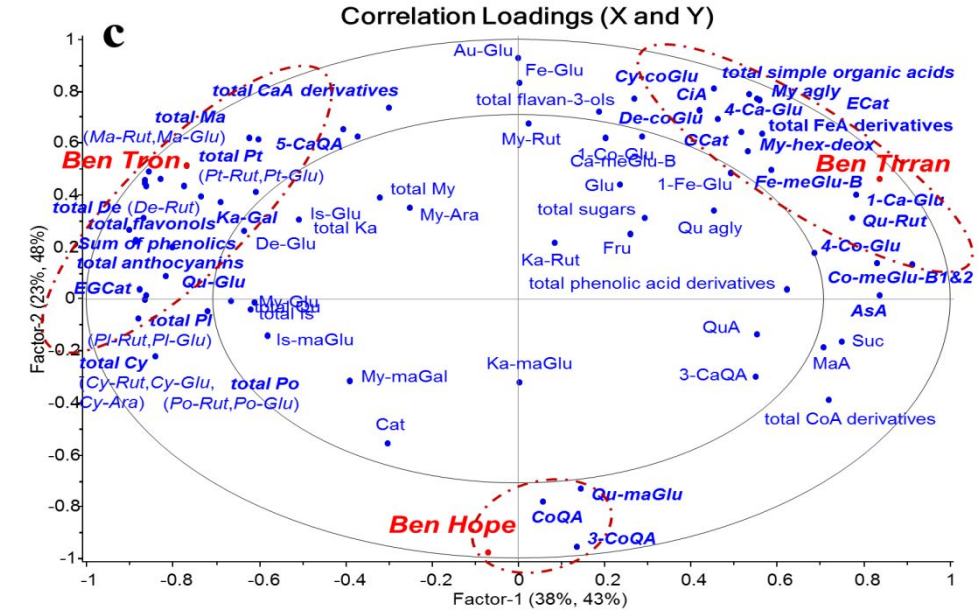
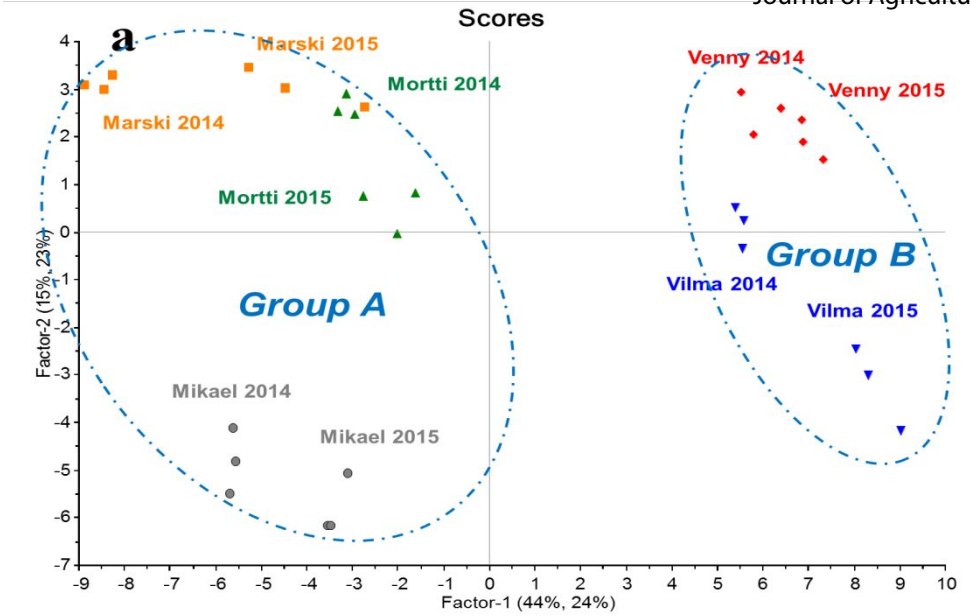
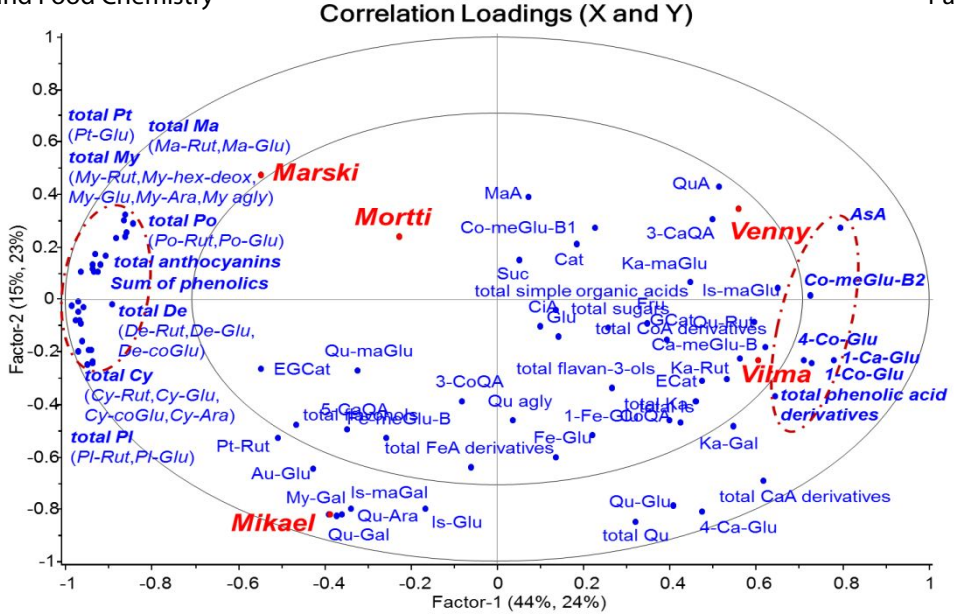
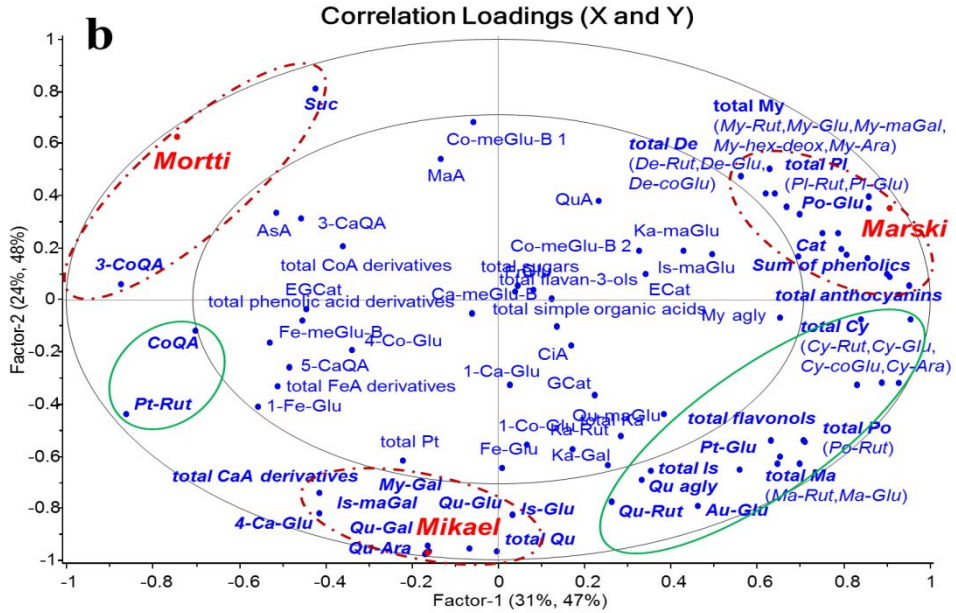

c
Correlation Loadings (X and Y)
Factor-2 (23%, 48%)
Factor-1 (38%, 43%)
Ben Tron
Ben Tirran
Ben Hope
Au-Glu
Fe-Glu
Cy-coGlu
total simple organic acids
total CaA derivatives
total flavan-3-ols
CiA
My agly
ECat
total Ma
(Ma-Rut,Ma-Glu)
De-coGlu
4-Ca-Glu
5-CaQA
My-Rut
total FeA derivatives
SCat
My-hex-deox
total Pt
(Pt-Rut,Pt-Glu)
1-Co-Glu
Ca-meGlu-B
Fe-meGlu-B
total My
Glu
1-Fe-Glu
1-Ca-Glu
total De (De-Rut)
My-Ara
total sugars
Qu agly
Qu-Rut
Ka-Gal
Is-Glu
total Ka
total flavonols
Fru
4-Co-Glu
Sum of phenolics
De-Glu
Ka-Rut
total anthocyanins
total phenolic acid derivatives
Co-meGlu-B1&2
Qu-Glu
EGCat
My-Glu
AsA
total Pl
(Pl-Rut,Pl-Glu)
Is-maGlu
QuA
Suc
total Cy
Ka-maGlu
MaA
(Cy-Rut,Cy-Glu,
Cy-Ara)
total Po
(Po-Rut,Po-Glu)
My-maGal
3-CaQA
Cat
total CoA derivatives
Qu-maGlu
CoQA
3-CoQA

Figure 4


a
Scores
Marski 2015
Marski 2014
Mortti 2014
Mortti 2015
Venny 2014
Venny 2015
Vilma 2014
Vilma 2015
Group A
Group B
Mikael 2014
Mikael 2015
Factor-2 (15%, 23%)
Factor-1 (44%, 24%)


Correlation Loadings (X and Y)
total Pt (Pt-Glu)
total Ma (Ma-Rut,Ma-Glu)
total My (My-Rut,My-hex-deox, My-Glu,My-Ara,My agly)
Marski
Mortti
Venny
Vilma
Mikael
MaA
QuA
AsA
Co-meGlu-B1
3-CaQA
Cat
Suc
Ka-maGlu
Is-maGlu
CiA
Glu
total sugars
total CoA derivatives
Ca-meGlu-B
Co-meGlu-B2
4-Co-Glu
1-Ca-Glu
1-Co-Glu
total phenolic acid derivatives
total Po (Po-Rut,Po-Glu)
total anthocyanins
Sum of phenolics
total De (De-Rut,De-Glu, De-coGlu)
Qu-maGlu
EGCat
3-CoQA
Qu agly
total flavan-3-ols
Ka-Rut
ECat
total Cy (Cy-Rut,Cy-Glu, Cy-coGlu,Cy-Ara)
5-CaQA
total Pl (Pl-Rut,Pl-Glu)
Pt-Rut
total FeA derivatives
Fe-Glu
Ka-Gal
Au-Glu
My-Gal
Is-maGal
Qu-Ara
Is-Glu
Qu-Gal
Qu-Glu
total CaA derivatives
total Qu
4-Ca-Glu
Factor-2 (15%, 23%)
Factor-1 (44%, 24%)


b
Correlation Loadings (X and Y)
Suc
Mortti
Marski
3-CoQA
CoQA
Pt-Rut
total My (My-Rut,My-Glu,My-maGal, My-hex-deox,My-Ara)
total De (De-Rut,De-Glu, De-coGlu)
total Pl (Pl-Rut,Pl-Glu)
Po-Glu
Co-meGlu-B 1
MaA
QuA
AsA
3-CaQA
Ka-maGlu
Co-meGlu-B 2
Cat
Sum of phenolics
total CoA derivatives
total sugars
total flavan-3-ols
Is-maGlu
ECat
Ca-meGlu-B
total anthocyanins
total phenolic acid derivatives
total simple organic acids
My agly
total Cy (Cy-Rut,Cy-Glu, Cy-coGlu,Cy-Ara)
Fe-meGlu-B
4-Co-Glu
CiA
5-CaQA
1-Ca-Glu
GCat
total FeA derivatives
1-Fe-Glu
Qu-maGlu
1-Co-Glu
Ka-Rut
total flavonols
total Po (Po-Rut)
total Pt
Fe-Glu
Ka-Gal
Pt-Glu
total Is
Qu agly
total Ma (Ma-Rut,Ma-Glu)
total CaA derivatives
My-Gal
Is-maGal
Qu-Glu
Is-Glu
Qu-Rut
Au-Glu
4-Ca-Glu
Qu-Gal
Mikael
Qu-Ara
total Qu
Factor-2 (24%, 48%)
Factor-1 (31%, 47%)

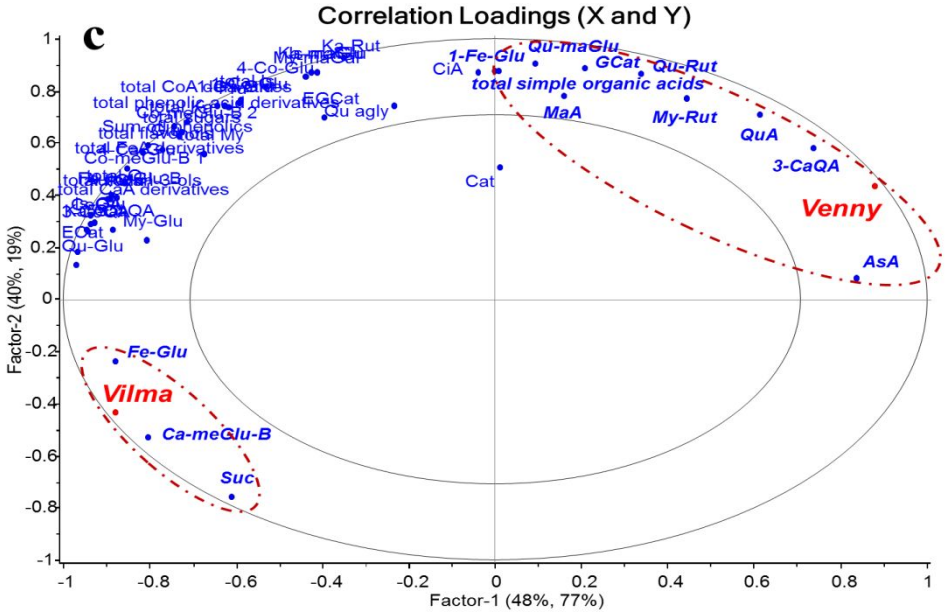

c
Correlation Loadings (X and Y)
1-Fe-Glu
Qu-maGlu
GCat
Qu-Rut
CiA
total simple organic acids
MaA
My-Rut
QuA
3-CaQA
Venny
AsA
Cat
Fe-Glu
Vilma
Ca-meGlu-B
Suc
Factor-2 (40%, 19%)
Factor-1 (48%, 77%)

Figure 5

Graphic for table of contents