On-Line Supplementary Material

Identification of Flavonoid and Phenolic Antioxidants in Blackcurrants, Blueberries, Raspberries, Redcurrants and Cranberries

Gina Borges, Alexandra Degeneve, William Mullen, and Alan Crozier

Plant Products and Human Nutrition Group, Graham Kerr Building, Division of Ecology and Evolutionary Biology, Faculty of Biomedical and Life Sciences, University of Glasgow, Glasgow G12 8QQ, UK

Berries for this study were purchased from local supermarkets in Glasgow. Extraction method and HPLC-PDA-MS^3 conditions are described in the text of Borges et al. (*1*). Samples were analysed with the mass spectrometer operating in full scan, negative and positive ionisation modes. Identifications were based on mass spectra, absorbance spectra and co-chromatography with standards. Where standards were not available identifications were assisted by the data of Baldi et al. *(2),* Goiffon et al. *(3, 4),* Prior et al. *(5),* Maatta, et al. *(6),* Maatta-Riihinen et al. *(7)* and Mullen et al. *(8, 9, 10)* among others. These publications provided information on the reverse-phase HPLC elution order of anthocyanidins, anthocyanins with different conjugated sugar moieties, flavonols and other phenolics.

Some of general rules for reversed phase HPLC elution order related to structure have been established although there will be variations depending upon the support and mobile phase used. They are:

i) The elution order of the anthocyanidins is delphinidin > cyanidin > pelargonidin > petunidin > peonidin followed by malvidin *(3, 11, 12).*

ii) The order of elution of anthocyanins conjugated with different sugars at the 3-position with different conjugated sugars is generally galactoside > glucoside > rutinoside > arabinoside *(3).*

iii) In general, as the degree of glycosylation of the conjugate increases, the anthocyanins are less well retained and have shorter retention times. The presence of a hydrophobic methyl group in the rhamnose molecules affects the chromatographic behaviour as cyanidin-3-*O*-rutinoside elutes after cyanidin-3-*O*-glucoside *(3)* and cyanidin-3-*O*-(2"-*O*-

glucosyl)rutinoside elutes after cyanidin-3-*O*-sophoroside and likewise the equivalent pelargonidin derivatives *(14).* A very marked increase in retention time is observed with acetylated anthocyanins such as delphinidin-3-*O*-(6''-*O*-acetyl)glucoside *(2).*

iv) For flavonol conjugates the sequence of elution has been reported by Rommel and Wrolstad *(14),* Zafrilla et al. *(15),* Mullen et al. *(8, 9, 10, 13)* and Marks et al. *(16).* In summary, the order of elution for quercetin conjugates is galactosylrhamnoside > rutinoside > galactoside > glucoside > pentoside. For kaempferol conjugates, the order is similar however, in this case the galactoside seemingly elutes before the rutinoside.

The HPLC peak numbers referred to are those assigned in the HPLC traces illustrated in **Figures 1-5** in the paper on berry antioxidants by Borges et al. *(1)* and in **Tables S1-S5** in this document.

Blackcurrants

The HPLC traces at 520 and 365 nm in **Figure 1** of the text revealed the presence of 18 peaks in the blackcurrant extract that were identified or partially identified by MS on the basis of the data presented in **Table S1**.

Peak 1 (retention time (t_R) – 12.9 min, λ_{max} - 330 nm) had a negatively charged molecular ion ($[M-H]^-$) at *m/z* 341 and a MS^2 ion at *m/z* 179. The *m/z* 179 fragment corresponds to the aglycone caffeic acid produced by a 162 *amu* cleavage of a hexose moiety. Based on the mass spectral and absorbance data as well as previously published reports *(6, 18),* this compound is identified as caffeic acid-*O*-glucoside

Peak 2 (t_R – 13.5 λ_{max} - 520 nm) had a positively charged molecular ion ($[M+H]^+$) at *m/z* 465, which yielded a MS^2 fragment at *m/z* 303 (delphinidin, ($[M+H]^+$–162, loss of a hexose moiety). This was identified as delphinidin-3-*O*-galactoside, which elutes before delphinidin-3-*O*-glucoside, peak 3.

Peak 3 (t_R – 14.8 λ_{max} - 520 nm) had also a $[M+H]^+$ at *m/z* 465, which yielded a MS^2 fragment at *m/z* 303 (delphinidin, $[M+H]^+$–162, loss of a hexose moiety). This peak was

identified as delphinidin-3-*O*-glucoside and this was confirmed by co-chromatography with a standard. This glucoside is a known component of blackcurrants *(3, 18, 19).*

Peak 4 (t_R – 17.0 min, λ_{max} - 520 nm) had a $[M+H]^+$ at *m/z* 611 which fragmented to produce MS^2 ions at *m/z* 465 ($[M+H]^+$–146, loss of a rhamnosyl moiety) and *m/z* 303 ($[M+H]^+$-308, cleavage of rhamnosyl and glucosyl units). Based on the fragment pattern it was identified as delphinidin-3-*O*-rutinoside, a known major anthocyanin in blackcurrants *(6, 19).*

Peak 5 (t_R – 18.3 min, λ_{max} - 520 nm) yielded a MS containing a $[M+H]^+$ at *m/z* 449, which fragmented on MS^2 to produce a cyanidin ion at *m/z* 287 ($[M+H]^+$-162, loss of a hexose moiety). This peak is cyanidin-3-*O*-glucoside and the identification was confirmed by co-chromatography with a standard.

Peak 6 (t_R – 20.3 min, λ_{max} - 520 nm) was identified as cyanidin-3-*O*-rutinoside. It had a $[M+H]^+$ at *m/z* 595 which fragmented to produce MS^2 ions at *m/z* 449 ($[M+H]^+$-146, loss of a rhamnose moiety) and *m/z* 287 ($[M+H]^+$-308, cleavage of rhamnose and glucose units).

Peak 7 (t_R – 22.4 min, λ_{max} - 520 nm) contained two anthocyanins. One had a $[M+H]^+$ at *m/z* 463, which on MS^2 yielded a fragment ion at *m/z* 301 (peonidin, $[M+H]^+$–162, loss of an hexose moiety). As this peak was the first eluted of three peonidin hexose conjugates (see peak 8 and 9) it was tentatively identified as peonidin-3-*O*-galactoside. The second compound had a $[M+H]^+$ at *m/z* 625, which yielded MS^2 fragments at *m/z* 479 ($[M+H]^+$–146, loss of rhamnose) and *m/z* 317 (petunidin, $[M+H]^+$–308, loss of rhamnose and glucose moieties). This corresponded with the fragmentation pattern of petunidin-3-*O*-rutinoside, previously reported to occur in blackcurrants *(19).*

Peak 8 (t_R – 24.0 min, λ_{max} - 520 nm) also contained two anthocyanins. The MS of this peak contained an ion at *m/z* 493 which fragmented on MS^2 to produce an ion at *m/z* 331 (malvidin, $[M+H]^+$–162, loss of an hexose unit), tentatively identified as malvidin-3-*O*-galactoside because of a similar retention time as peak 7 identified in blueberries (**Table S2**). The second compound in peak 8 was identified as peonidin-3-*O*-glucoside based on its mass spectrum ($[M+H]^+$ at *m/z* 463 and a MS^2 ion at *m/z* 301), its elution order and previous published data *(19).*

Peak 9 (t_R – 25.9 min, λ_{max} - 525 nm) was identified as peonidin-3-*O*-rutinoside, a known component of blackcurrants *(19),* on the basis of a $[M+H]^+$ at *m/z* 609, which yielded a MS^2 peonidin fragment ion at *m/z* 301 formed by the successive cleavage of a rhamnose and a glucose unit.

Peak 10 (t_R – 31.3 min, λ_{max} - 355 nm) yielded a $[M-H]^-$ at *m/z* 625 and MS^2 fragments at *m/z* 317 (myricetin, $[M-H]^-$–308, loss of a rutinosyl moiety). It is, therefore, identified as myricetin-3-*O*-rutinoside, previously identified in blackcurrant extract *(6).*

Peak 11 (t_R – 31.8 min, λ_{max} - 355 nm) is a myricetin-*O*-glucuronide conjugate, having a $[M-H]^-$ at *m/z* 493, which with neutral loss of 176 *amu* yielded a MS^2 fragment corresponding to myricetin at *m/z* 317.

Peak 12 (t_R – 35.0 min, λ_{max} - 355 nm) produced a $[M+H]^+$ at *m/z* 567 which on MS^2 yielded a fragment at *m/z* 319 via a loss of 248 *amu*. According to Maatta et al. *(6)* this corresponds to the loss of a malonylglucoside unit with the fragmentation pattern being indicative of the occurrence of myricetin-3-*O*-(6''-*O*-malonyl)glucoside. When analysed with negative ionisation no $[M-H]^-$ was apparent instead an ion at *m/z* 521 was observed which fragmented in MS^2 to produce myricetin ion at *m/z* 317, through a loss of 204 *amu*. The loss of 45 *amu* to produce the *m/z* 521 ion equates with the loss of the carboxyl function from the malonyl unit.

Peak 13 (t_R – 37.5 min, λ_{max} - 350 nm) had a $[M-H]^-$ at *m/z* 609 which yielded a MS^2 ion at *m/z* 301 (quercetin, $[M-H]^-$-308, loss of a rutinose unit). Based on this MS spectrum and co-chromatography with a reference compound, this compound was identified as quercetin-3-*O*-rutinoside, previously detected in blackcurrants *(6).*

Peak 14 (t_R – 39.1 min, λ_{max} - 350 nm) produced a typical quercetin-*O*-hexoside mass spectrum ($[M-H]^-$ at *m/z* 463, MS^2 at 301). Peak 14 was identified as quercetin-3-*O*-glucoside through co-chromatography with a reference compound.

Peak 15 (t_R – 40.5 min, λ_{max} - 525 nm) was a minor anthocyanin with a $[M+H]^+$ at *m/z* 611 and a MS^2 delphinidin fragment ion at *m/z* 303 produced by cleavage of a 308 *amu*. This compound was strongly retained on the column. Slimestadt et al*. (19)* reported the

presence of delphinidin conjugate with similar properties (MS^2, absorption and late t_R). This compound was, therefore, tentatively identified as delphinidin-3-*O*-(6''-*O*-coumaroyl)glucoside.

Peak 16 (t_R – 42.5 min, λ_{max} - 350 nm) yielding the same $[M-H]^-$ and MS^2 fragments as myricetin-3-*O*-(6”-*O*-malonyl)glucoside (peak 12), but at *m/z* values 16 *amu* lower indicative of the presence of quercetin-3-*O*-(6''-*O*-malonyl)glucoside. The occurrence of this compound has been reported in blackcurrants *(6, 7).*

Peak 17 (t_R – 43.9 min, λ_{max} - 315 nm) produced a $[M-H]^-$ at *m/z* 593 and MS^2 fragment at *m/z* 285. The *m/z* 285 ion, produced by a 308 *amu* loss of rhamnose and glucose, corresponded to the aglycone kaempferol. This compound was identified as kaempferol-3-*O*-rutinoside, which has been reported to occur in blackcurrants *(6).*

Peak 18 (t_R – 45.2 min, λ_{max} - 340 nm) was tentatively identified as kaempferol-3-*O*-galactoside. It yielded a $[M-H]^-$ at *m/z* 447 and an MS^2 fragment at *m/z* 285 after a 162 *amu* loss corresponding to cleavage of a hexose unit but did not co-chromatograph with kaempferol-3-*O*-glucoside.

Blueberries

HPLC-PDA-MS^2 analysis resulted in the identification of 18 phenolic compounds in blueberries (**Figure 2**). The data are summarised in **Table S2**. Unlike the earlier published analysis of blackcurrants that aided identification, a number of studies with blueberry have analysed samples as aglycones after acid/enzyme hydrolysis *(20, 21, 22).* As such they were of limited value, in contrast to the investigations of Goiffon et al*. (4)* and Prior et al. *(5)* which analysed unhydrolysed blueberry extracts.

Peak 1 (t_R – 13.5 min, λ_{max} 520 nm) had $[M+H]^+$ at *m/z 4*65, which on MS^2 yielded a fragment ion at *m/z* 303 (delphinidin, $[M+H]^+$–162, loss of a hexosyl unit). Based on the mass spectra data and HPLC elution properties, peak 1 was identified as delphinidin-3-*O*-galactoside, a major anthocyanin in blueberry *(4, 5).*

Peak 2 (t_R – 14.8 min, λ_{max} 520 nm) had $[M+H]^+$ at *m/z* 465, which on MS^2 yielded a fragment ion at *m/z* 303 (delphinidin, $[M+H]^+$–162, loss of a hexose unit). Based on the mass spectral data and co-chromatography with standard, peak 2 was identified as delphinidin-3-*O*-glucoside**.**

Peak 3 (t_R – 16.7 min, λ_{max} – 520 nm) contained two components. One had a $[M+H]^+$ at *m/z* 449 which on MS^2 produced a fragment at *m/z* 287 (cyanidin, $[M+H]^+$-162, corresponding to the cleavage of an hexose unit). This compound, which eluted before a cyanidin-3-*O*-glucoside standard, was identified as cyanidin-3-*O*-galactoside, a known component of blueberries (4, 5). The second compound had a $[M+H]^+$ at *m/z* 435, which yielded on MS^2 fragment at *m/z* 303 (delphinidin, $[M+H]^+$–132, loss of a pentose group). This compound was therefore delphinidin-3-*O*-arabinoside, also previously identified in blueberries *(4, 5).*

Peak 4 (t_R – 19.4 min, λ_{max} – 520 nm) had a $[M+H]^+$ at *m/z* 479 which on MS^2 produced a fragment ion corresponding to petunidin at *m/z* 317 via a 162 *amu* loss of a hexose unit. The presence of both petunidin-3-*O*-galactoside and petunidin-3-*O*-glucoside has been reported in blueberry *(4),* but as this compound eluted before cyanidin-3-*O*-arabinoside (peak 5), peak 4 was more likely to be petunidin-3-*O*-galactoside.

Peak 5 (t_R – 20.2 min, λ_{max} – 515 nm) had a $[M+H]^+$ at *m/z* 419 and a MS^2 cyanidin fragment at *m/z* 287 produced by cleavage of a pentose moiety. This peak was, therefore, identified as cyanidin-3-*O*-arabinoside a known blueberry anthocyanin *(4, 5).*

Peak 6 (t_R – 22.4 min, λ_{max} – 520 nm) contained two anthocyanins. One was identified as petunidin-3-*O*-arabinoside, which has been identified in blueberry in previous studies *(4, 5)*. It had a $[M+H]^+$ at *m/z* 449 which fragmented to produce MS^2 ions at *m/z* 317 (petunidin, $[M+H]^+$–132, loss of a pentose unit). The MS of this peak also contained an ion at *m/z* 463, which on MS^2 produced a peonidin fragment at *m/z* 301 ($[M+H]^+$–162, loss of an hexose unit). This compound was identified as peonidin-3-*O*-galactoside, rather than peonidin-3-*O*-glucoside by comparison with a standard.

Peak 7 (t_R – 24.0 min, λ_{max} – 520 nm) had a $[M+H]^+$ at *m/z* 493 which on MS^2 produced an ion at *m/z* 331 (malvidin, $[M+H]^+$–162, loss of an hexose). On the basis of this

mass spectral data, elution prior to malvidin-3-*O*-glucoside (see peak 8) and previous studies *(4, 5)* this compound was identified as malvidin-3-*O*-galactoside**.**

Peak 8 (t_R – 24.7 min, λ_{max} – 525 nm) contained two anthocyanins. One, like peak 7, had a $[M+H]^+$ at *m/z* 493 and yielded a similar MS^2 fragmentation pattern. This compound was identified as malvidin-3-*O*-glucoside, a known anthocyanin in blueberries *(4, 5).* The identification was confirmed by co-chromatography with a standard. The other component had a $[M+H]^+$ at *m/z* 507 which on MS^2 produced a fragment ion corresponding to delphinidin at *m/z* 303. The 204 *amu* loss equates with cleavage of acetyl and glucosyl units. This mass spectral fragmentation pattern is in keeping with the presence of delphinidin-3-*O*-(6''-*O*-acetyl)glucoside, an endogenous anthocyanin of low bush blueberry *(5).*

Peak 9 (t_R – 25.7 min, λ_{max} – 525 nm) was a minor anthocyanin with a $[M+H]^+$ at *m/z* 433 and a MS^2 peonidin fragment at *m/z* 301 produced by the cleavage of a pentose unit. On the basis the mass spectrum and previously published data *(4, 5),* this peak is identified as peonidin-3-*O*-arabinoside.

Peak 10 (t_R – 27.4 min, λ_{max} – 525 nm) which had a $[M+H]^+$ at *m/z* 463 that fragmented to produce a MS^2 ion at *m/z* 331 ($[M+H]^+$–132, loss of a pentose unit) was identified as malvidin-3-*O*-arabinoside, which has been detected in blueberries in earlier studies *(4, 5).*

Peak 11 (t_R – 30.4 min, λ_{max} – 525 nm) was a minor anthocyanin. It had a $[M+H]^+$ at *m/z* 521 which fragmented to produce an MS^2 ion at *m/z* 317 ($[M+H]^+$–204, loss of acetyl and glucosyl units). This mass spectrum indicated the presence of petunidin-3-O-(6''-O-acetyl)glucoside, a known low bush blueberry anthocyanin *(5).*

Peak 12 (t_R – 30.9 min, λ_{max} – 355 nm) had a $[M-H]^-$ at *m/z* 479 which with neutral loss of a 162 *amu* hexose unit yielded a MS^2 fragment corresponding to myricetin at *m/z* 317. It was therefore a myricetin-*O*-hexose conjugate, probably myricetin-3-*O*-galactoside as this compound have been reported previously to occur in blueberries *(7).*

Peak 13 (t_R – 33.8 min, λ_{max} – 325-355 nm) contained two compounds. One had a $[M-H]^-$ at *m/z* 625 with neutral loss of a 324 *amu* (cleavage of two hexose units) yielded a MS^2 fragment corresponding to quercetin at *m/z* 301. It is, therefore, a quercetin-O-

diglucoside. The other component had a $[M-H]^-$ at *m/z* 367 which on MS^2 produced fragment at *m/z* 191, 179 and 135. Based on MS data, in agreement with the mass spectral key of Clifford et al*. (23),* this compound was identified as 5-*O*-feruloylquinic acid.

Peak 14 (t_R – 35.5 min, λ_{max} – 530 nm) was a minor anthocyanin. It had a $[M+H]^+$ at *m/z* 535 and the same loss of a 204 *amu* as in peak 8 and 11. It was therefore identified as malvidin-3-*O*-(6''-*O*-acetyl)glucoside, as its presence having been detected previously in lowbush blueberry by Prior et al. *(5).*

Peak 15 (t_R – 37.5 min, λ_{max} – 355 nm) had a $[M-H]^-$ at *m/z* 609, which on MS^2 yielded a quercetin-like fragment at *m/z* 301. The 308 *amu* loss corresponds to cleavage of a hexose and rhamnose unit. This indicates the presence of quercetin-3-*O*-rutinoside, which was confirmed by co-chromatography with a standard.

Peak 16 (t_R – 38.1 min, λ_{max} – 355 nm) contained an ion at *m/z* 463, which produced on MS^2 a quercetin fragment at *m/z* 301. This compound, which eluted before a quercetin-3-*O*-glucoside standard, was identified as quercetin-3-*O*-galactoside, a known constituent of blueberries *(7).*

Peak 17 (t_R – 39.2 min, λ_{max} – 355 nm) is a flavonol with a $[M-H]^-$ at *m/z* 463, which with loss of 162 *amu* yielded a MS^2 fragment at *m/z* 301 corresponding to quercetin. It was identified as quercetin-3-*O*-glucoside, as it co-eluted with a standard.

Peak 18 (t_R – 43.0 min, λ_{max} – 355 nm) contained two compounds. One had a $[M-H]^-$ at *m/z* 433, which yielded a MS^2 fragment at *m/z* 301 ($[M-H]^-$–132, loss of a pentose unit) and MS^3 ions at *m/z* 271, 255 and 179. It is, therefore, a quercetin-*O*-pentose conjugate, possibly quercetin-3-*O*-arabinoside, as this compound has previously been identified in blueberries *(7).* The second compound had $[M+H]^+$ at *m/z* 505 and the same loss of a 204 *amu* as in peak 8, 11 and 14. It was therefore identified as quercetin-3-*O*-(6''-*O*-acetyl)glucoside.

Raspberries

HPLC-PDA-MS^3 analysis of raspberries resulted in the identification of 15 phenolic compounds (**Figure 3**), on the basis of data summarised in **Table S3**. Where reference compounds were not available identifications were made by comparison with earlier data on raspberry anthocyanins and data on the MS fragmentation patterns of anthocyanins and the *m/z* losses associated with cleavage of various sugars and other substituent groups presented by Goiffon et al. *(4)* and Giusti et al. *(24).* Similarly, the data of Rommel and Wrolstad *(14)* and Zafrilla *et al*. *(15)* aided the MS-based identifications of flavonols and ellagic acid sugar conjugates. Ellagitannin identification was based on Mullen et al*. (10, 13, 25).*

Peak 1 (t_R – 16.1 min, λ_{max} – 515 nm) had a $M+H]^+$ at *m/z* 611, which on MS^2 produced a fragment ion corresponding to cyanidin at *m/z* 287. The 324 *amu* loss equates with cleavage of a sophorose unit, which consists of two glucose moieties. This peak, therefore was identified as cyanidin-3-*O*-sophoroside, which is the major anthocyanin in raspberries.

Peak 2 (t_R – 18.0 min, λ_{max} – 515 nm) contained three anthocyanins. One was identified as cyanidin-3-O-(2''-*O*-glucosyl)rutinoside, which has been detected in a previous study with raspberries (25). It had a $[M+H]^+$ at *m/z* 757 which fragmented to produce MS^2 ions at *m/z* 611 ($[M+H]^+$–146, loss of a rhamnose moiety) and *m/z* 287 ($[M+H]^+$–470 corresponding to the cleavage of one rhamnose and two hexose units). The MS of this peak also contained an ion at *m/z* 581 which fragmented on MS^2 to produce a minor ion at *m/z* 449 ($[M+H]^+$–132, loss of a xylose group) and a major fragment at *m/z* 287 ($[M+H]^+$–132–162, loss of xylose and hexose units). This compound is the xylosyl-glucoside, cyanidin-3-*O*-sambubioside, a known raspberry anthocyanin *(13).* The third anthocyanin was cyanidin-3-*O*-glucoside which had a $[M+H]^+$ at *m/z* 449 which on MS^2 yielded a cyanidin fragment ion at *m/z* 287 formed by the cleavage of a 162 *amu* hexose unit. A cyanidin-3-*O*-glucoside standard co-chromatographed with the 520 nm peak 2. Cyanidin-3-*O*-glucoside is a known constituent of raspberries *(13).*

Peak 3 (t_R – 18.9 min, λ_{max} – 500 nm) was a minor anthocyanin with a $[M+H]^+$ at *m/z* 595 and a MS^2 pelargonidin fragment ion at *m/z* 271 produced by cleavage of a 324 *amu* sophorose unit. This compound was therefore identified as pelargonidin-3-*O*-sophoroside detected in raspberries in earlier studies *(4, 13).*

Peak 4 (t_R – 20.3 min, λ_{max} – 510 nm) was an anthocyanin with a $[M+H]^+$ at *m/z* 595 which on MS^2 produced a minor fragment at *m/z* 449 ($[M+H]^+$–146, loss of rhamnose) and a major fragment at *m/z* 287 (cyanidin, $[M+H]^+$–308, corresponding to cleavage of a rhamnose unit and a glucose moiety). This compound was, therefore, cyanidin-3-*O*-rutinoside.

Peak 5 (t_R – 21.2 min, λ_{max} - 500 nm) contained two compounds. One had a $[M+H]^+$ at *m/z* 433 which on MS^2 produced a pelargonidin fragment ion at *m/z* 271 via a 162 *amu* cleavage of a glucose unit. This compound was pelargondin-3-*O*-glucoside, a known endogenous raspberry anthocyanin *(13).* The second compound was also an anthocyanin. It had a $[M+H]^+$ at *m/z* 741, which after a 470 *amu* loss corresponding to cleavage of xylose and rutinose moieties, yielded a pelargonidin MS^2 ion at *m/z* 271. This compound was, therefore pelargonidin-3-*O*-(2''-*O*-glucosyl)rutinoside *(13).*

Peak 6 (t_R – 29.6 min, λ_{max} - 250 nm) had a $[M-H]^-$ at *m/z* 1401, reported to be doubly charged, with a true mass of 2804 (*10*). Again MS^2 of the doubly charged ion produced a range of fragments at *m/z* 1869, *m/z* 1567 (1869-302), loss of hexhydroxydiphenoyl unit, *m/z* 1265, *m/z* 935 and *m/z* 633. This peak was the ellagitannin lambertianin C, which has previously been detected in extracts of raspberry leaves *(27)* and fruit *(10).*

Peak 7 (t_R – 30.8 min, λ_{max} - 250 nm), the major component in the raspberry extract had a $[M-H]^-$ at *m/z* 1869 which on MS^2 yielded fragment ions very similar to those produced by lambertianin C with ions at *m/z* 1567, 1265, 933 and 631. The mass spectrum and retention properties match those of sanguiin H-6 *(10).*

Peak 8 (t_R – 32.7 min, λ_{max} - 360 nm) had a $[M-H]^-$ at *m/z* 433 and MS^2 yielded an ion at *m/z* 301 ($[M-H]^-$–132, loss of a pentosyl unit) and MS^3 produced a *m/z* 257 fragment indicating the presence of ellagic acid rather than quercetin (*10*). This compound was, therefore, an ellagic acid-*O*-pentose conjugate.

Peak 9 (t_R – 33.5 min, λ_{max} - 360 nm) had a $[M-H]^-$ at *m/z* 433 and MS^2 yielded an ion at *m/z* 301 ($[M-H]^-$-132, loss of a pentosyl unit) and MS^3 produced a *m/z* 257 fragment indicating the presence of ellagic acid. This compound was, therefore, another ellagic acid-*O*-pentose conjugate.

Peak 10 (t_R – 34.4 min, λ_{max} - 360 nm) produced a $[M-H]^-$ at *m/z* 301 and MS^2 ionisation yielded a fragment at *m/z* 257, which matches the mass spectrum of ellagic acid. This identification was confirmed by co-chromatography with a reference compound.

Peak 11 (t_R – 35.8 min, λ_{max} - 340 nm) had a mass spectra with a $[M-H]^-$ at *m/z* 609, which yielded a MS^2 fragment at *m/z* 301 which in this instance corresponds to loss of hexose and rhamnose units ($[M-H^-$-308). Peak 11 was, therefore, the quercetin-*O*-galactosylrhamnoside previously detected in raspberries *(13).*

Peak 12 (t_R – 37.4 min, λ_{max} - 340 nm) had identical mass spectra than peak 11, a $[M-H]^-$ at *m/z* 609, which yielded a MS^2 fragment at *m/z* 301. In keeping with this fragmentation pattern this peak co-chromatographed with a quercetin-3-*O*-rutinoside standard. Previous analytical work with raspberries has shown that quercetin-3-*O*-rutinoside elutes after the quercetin-*O*-galactosylrhamnoside peak (peak 9) *(25).*

Peak 13 (t_R – 37.7 min, λ_{max} - 340 nm) is a quercetin hexose, having a $[M-H]^-$ at *m/z* 463, which with neutral loss of 162 *amu* yielded a MS^2 fragment corresponding to quercetin at *m/z* 301. This compound, which eluted before a quercetin-3-*O*-glucoside standard, was identified as quercetin-3-*O*-galactoside.

Peak 14 (t_R – 39.2 min, λ_{max} - 340 nm) had a $[M-H]^-$ at *m/z* 463 which on MS^2 yielded an ion at *m/z* 301 which with neutral loss of 162 *amu* yielded a MS^2 fragment corresponding to quercetin at *m/z* 301. The MS data, and co-chromatography with a standard, indicate the presence of a quercetin-3-*O*-glucoside.

Peak 15 (t_R – 42.5 min, λ_{max} - 360 nm) had both a $[M-H]^-$ at *m/z* 475, which yielded MS^2 fragments at *m/z* 301 ($[M-H]^-$-174, loss of acetylpentose). Mullen et al. *(10)* have tentatively identified it as ellagic acid-4-*O*-acetylxyloside. These compound previously have been detected in raspberries by Zafrilla et al. *(15).*

Redcurrants

The HPLC traces obtained at 520, 365 and 280 nm indicate the 13 compounds identified in redcurrants (**Figure 4**). The identification of these compounds is summarised below and in **Table S4**.

Peak 1 (t_R – 9.1 min, λ_{max} - 260 nm) had a $[M-H]^-$ at *m/z* 299 and MS^2 yielded an ion at *m/z* 137 ($[M-H]^-$-162, loss of an hexose unit). This compound was tentatively identified as a 4-hydroxybenzoic acid-*O*-hexose conjugate, in agreement with Maatta et al. *(27)* who identified 4-hydroxybenzoic acid after acid hydrolysis of a redcurrant extract.

Peas 2 (t_R – 12.8 min, λ_{max} - 330 nm) had both a $[M-H]^-$ at *m/z* 341 which on MS^2 yielded a fragment releasing an ion at *m/z* 179. The *m/z* 179 ion is the aglycone caffeic acid produced by a loss of 162 *amu*, which corresponds with the cleavage of a hexose moiety. Based on the mass spectral and PDA data and previously published information *(17),* this compounds was identified as caffeic acid-*O*-glucoside present also in blackcurrant (peak 1).

Peak 3 (t_R – 18.0 min, λ_{max} - 515 nm) had a $[M+H]^+$ at *m/z* 581 which on MS^2 produced a cyanidin fragment ion at *m/z* 287. The loss of 294 *amu* corresponds to the cleavage of a xylose and a hexose unit. The mass spectrum and the HPLC retention correspond to that of cyanidin-3-*O*-sambubioside, identified in redcurrants in earlier studies *(6, 28).*

Peak 4 (t_R – 20.3 min, λ_{max} - 515 nm) was the main peak present in the redcurrant extract and contained two compounds. The first had a $[M+H]^+$ at *m/z* 595 which on MS^2 produced a minor fragment at *m/z* 449 ($[M+H]^+$–146, loss of rhamnose unit) and a major fragment at *m/z* 287 (cyanidin, $[M+H]^+$–308 corresponding to the cleavage of rhamnose and glucose moieties). This compound was, therefore, cyanidin-3-*O*-rutinoside. The second compound had a $[M+H]^+$ at *m/z* 727, which yielded MS^2 fragments at *m/z* 581 ($[M+H]^+$–146, loss of rhamnose) and *m/z* 287 (cyanidin, $[M+H]^+$–440, loss of rhamnosyl, glucosyl and xylosyl groups). This corresponds to the fragmentation of cyanidin-3-*O*-(2''-xylosyl)rutinoside, which has previously been detected in redcurrants *(4, 6, 28).*

Peak 5 (t_R – 31.1 min, λ_{max} – 355nm) had a $[M-H]^-$ at *m/z* 625 which with the loss of 308 *amu* yielded an MS^2 fragment corresponding to myricetin at *m/z* 317. These spectra indicated the presence of a myricetin-*O*-rutinoside conjugate.

Peak 6 (t_R – 31.6, λ_{max} – 330 nm) yielded a $[M-H]^-$ at *m/z* 463 and MS^2 fragment at 317 ($[M-H]^-$-146, loss of a rhamnosyl moiety). It was, therefore, identified as a myricetin-*O*-rhamnoside.

Peak 7 (t_R – 37.4 min, λ_{max} – 355 nm) was identified as quercetin-3-*O*-rutinoside. It yielded a $[M-H]^-$ at *m/z* 609, which with neutral loss of 308 *amu* yielded a MS^2 fragment corresponding to quercetin at *m/z* 301.

Peak 8 (t_R – 38.0 min, λ_{max} – 355 nm) produced a typical quercetin hexose mass spectrum ($[M-H]^-$ at *m/z* 463, MS^2 at *m/z* 301 and MS^3 at *m/z* 271, 255 and main ion at *m/z* 179). Earlier elution than quercetin-3-*O*-glucoside (peak 9) indicates that this compound could be quercetin-3-*O*-galactoside.

Peak 9 (t_R – 39.1 min, λ_{max} – 355 nm) produced a typical quercetin glucoside mass spectrum ($[M-H]^-$ at *m/z* 463, MS^2 at *m/z* 301 and MS^3 at *m/z* 271, 255 and main ion at *m/z* 179). Co-chromatography established the presence of quercetin-3-*O*-glucoside.

Peak 10 (t_R – 43.0 min, λ_{max} 345 nm) had a $[M-H]^-$ at *m/z* 505 and MS^2 fragments at *m/z* 463 ($[M-H]^-$–42, loss of a malonic acid) and *m/z* 301 (quercetin, $[M-H]^-$–204). As in peak 16 in blackcurrants (see **Table S1**), the 204 *amu* loss corresponds to the loss of hexose and malonyl groups, which in negative ion mode lost the 45 *amu* carboxylic function from the pseudomolecular ion. This is indicative of the presence of a quercetin-*O*-malonyl-hexose conjugate. The presence of quercetin-3-*O*-(6''-*O*-malonyl)glucoside has previously been reported in redcurrants by Maatta et al. *(6).*

Peak 11 (t_R – 43.6 min, λ_{max} - 345 nm) yielded a $[M-H]^-$ at *m/z* 593 and an MS^2 fragment at *m/z* 285. The *m/z* 285 ion (kaempferol) was produced by a 308 *amu* cleavage, which corresponded to the loss of a rutinose unit. Peak 11, which co-chromatographed with peak 17 in blackcurrants, was therefore tentatively identified as kaempferol-3-*O*-rutinoside.

Peak 12 (t_R – 45.2 min, λ_{max} - 340 nm) had a $[M-H]^-$ at *m/z* 447 which with a loss of 162 *amu* (cleavage of hexose) produced a MS^2 fragment at *m/z* 285 (kaempferol). Earlier elution than kaempferol-3-*O*-glucoside (peak 13) and similar retention time of the peak 18 in blackcurrant established that this compound could be kaempferol-3-*O*-galactoside.

Peak 13 (t_R – 45.9 min, λ_{max} - 340 nm) had a $[M-H]^-$ at *m/z* 447 which with a loss of 162 *amu* (cleavage of hexose) produced a MS^2 fragment at *m/z* 285 (kaempferol). Co-elution with a standard established that this compound was kaempferol-3-*O*-glucoside.

Cranberries

The HPLC traces obtained at 520, 365 and 280 nm facilitated the detection of 18 phenolic compounds (**Figure 5**). Where standard compounds were unavailable, identifications were based on previously published analysis of cranberry extracts *(5, 7, 29).* The identifications of phenolic compounds are summarised in **Table S5**.

Peaks 1, 11 and 13 (t_R – 13.1, 32.7 and 37.7 min, λ_{max} - 290 nm) yielded a $[M-H]^-$ at *m/z* 577 and MS^2 fragments at *m/z* 425 and *m/z* 289 ($[M-H]^-$–288, loss of a catechin/epicatechin unit), characteristic of a procyanidin dimer.

Peak 2 (t_R – 16.8 min, λ_{max} - 515 nm) had a $[M+H]^+$ at *m/z* 449 which on MS^2 produced a fragment ion corresponding to cyanidin at *m/z* 287. The 162 *amu* loss equates with cleavage of a hexose unit. This compound was, therefore, identified as cyanidin-3-*O*-galactoside, one of the major anthocyanins in cranberries *(5).*

Peak 3 (t_R – 18.4 min) in negative ionisation revealed the presence of a $[M-H]^-$ at *m/z* 325, which on MS^2 yielded an *m/z* 163 fragment (coumaric acid, $[M-H]^-$–162, loss of an hexose moiety). This compound was, therefore, a *p*-coumaric acid-*O*-hexoside conjugate, which has been reported previously in cranberries *(7)*

Peak 4 (t_R – 20.3 min, λ_{max} - 515 nm) had a $[M+H]^+$ at *m/z* 419 which on MS^2 produced a fragment ion corresponding to cyanidin at *m/z* 287 via a 132 *amu* cleavage of a pentose unit. This compound was identified as cyanidin-3-*O*-arabinoside, a major anthocyanin present in cranberries *(5).*

Peak 5 (t_R – 21.7 min, λ_{max} - 280 nm) had a $[M-H]^-$ at *m/z* 289 which on MS^2 yielded a fragments of *m/z* 245. This fragmentation pattern is that of a flavan-3-ol monomer which co-chromatography with a standard identified, therefore, as (–)-epicatechin.

Peak 6 (t_R –22.4 min, λ_{max} - 515 nm) was a major anthocyanin with a $[M+H]^+$ at *m/z* 463 and a MS^2 peonidin fragment at *m/z* 301 produced by cleavage of a hexose moiety. This fragmentation pattern was in keeping with the presence of peonidin-3-*O*-galactoside, a known constituent of cranberries (*5*) that elutes before peonidin-3-*O*-glucoside (peak 7).

Peak 7 (t_R –24.2 min, λ_{max} - 280 and 520 nm) had a $[M+H]^+$ at *m/z* 463, which on MS^2 produced a fragment ion corresponding to peonidin at *m/z* 301 and a $[M+H]^+$-162, loss of a glucosyl unit. It was identified as peonidin-3-*O*-glucoside by co-chromatography with a standard.

Peak 8 (t_R –25.7 min, λ_{max} - 515 nm) had a $[M+H]^+$ at *m/z* 433, which yielded MS^2 fragments at *m/z* 301 (peonidin, a $[M+H]^+$-132, loss of a pentosyl unit). It was identified as a peonidin-*O*-arabinoside based on similar retention time as peak 9 in blueberries.

Peak 9 (t_R –27.4 min, λ_{max} - 520 nm) was a minor anthocyanin and had a $[M+H]^+$ at *m/z* 463 which with neutral loss of 162 *amu* yielded a MS^2 fragment corresponding to malvidin at *m/z* 331. This compound was a malvidin-*O*-pentose conjugate, possibly malvidin-3-*O*-arabinoside based on its retention time being the same as peak 10 in blueberries (see **Table S2**).

Peak 10 (t_R –30.9 min, λ_{max} - 355 nm) produced a $[M-H]^-$ at *m/z* 479 which with a loss of 162 *amu* yielded a MS^2 at *m/z* 317. It is, therefore, a myricetin-*O*-hexose conjugate, probably myricetin-3-*O*-galactoside a known cranberry flavonol *(29).*

Peak 12 (t_R –35.8 min, λ_{max} - 355 nm) was a myricetin pentose conjugate having a $[M-H]^-$ at *m/z* 449 and a MS^2 ion at *m/z* 317. This compound might be myricetin-3-arabinoside, which has been identified in cranberries by Vvedenskaya et al. *(29).*

Peak 14 (t_R – 38.2 min, λ_{max} - 355 nm) was the major flavonol present in cranberries and produced a mass spectrum characteristic of a quercetin hexose conjugate ($[M-H]^-$ at *m/z* 463, MS^2 ion at *m/z* 301 and MS^3 of this ion produced a major fragment at *m/z* 179). In view

of this mass spectrum, the high concentration and HPLC order of elution, this compound is probably quercetin-3-*O*-galactoside**,** previously detected in cranberries *(29).*

Peaks 15, 16 and 17 (t_R – 41.4, 43.2 and 43.8 min, λ_{max} - 355 and 350 nm) all had a $[M-H]^-$ at *m/z* 433 which, with neutral loss of a 132 *amu* pentose unit, yielded a MS^2 fragment corresponding to quercetin at *m/z* 301. These three flavonols are, therefore, all quercetin pentose conjugates. Based on their elution order they were identified as quercetin-3-*O*-xylopyranoside, quercetin-3-*O*-arabinopyranoside and quercetin-3-*O*-arabinofuranoside respectively, previously identified in a cranberry extract by HPLC-MS and NMR *(29).*

Peak 18 (t_R – 46.1 min, λ_{max} - 345 nm) had a $[M-H]^-$ at *m/z* 447 which yielded an MS^2 fragment at *m/z* 301 (quercetin), the $[M-H]^-$-146 loss corresponding to cleavage of a rhamnose unit. The mass spectral data and HPLC retention are in keeping with this peak being quercetin-3-*O*-rhamnoside, which was previously detected in cranberries *(29).*

LITERATURE CITED

1. Borges, G.; Mullen, W.; Degenevé, A.; Crozier, A. Analysis of berries by HPLC-PDA-MS^3 with on-line antioxidant detection. *J. Agric. Food Chem.* **2009**, submitted.

2. Baldi, A., Romani, A.; Mulinacci, N.; Vincieri, F.F.; Casetta, B. HPLC/MS application to anthocyanins of *Vitis vinifera* L. *J. Agric. Food Chem.* **1995**, 43, 2104-2109.

3. Goiffon, J.P.; Brun, M.; Bourrier, M.J. High-performance liquid chromatography of red fruit anthocyanins. *J. Chromogr.* **1991,** 537, 101-121.

4. Goiffon, J.P.; Mouly, P.P.; Gaydou, E.M.. Anthocyanic pigment determination in red fruit juices, concentrated juices and syrups using liquid chromatography *Anal. Chim. Acta.* **1999,** 382**,** 39-45.

5. Prior, R.L.; Lazarus, S.A.; Cao, G.; Muccitelli, H.; Hammerstone, J.F. Identification of procyanidins and anthocyanins in blueberries and cranberries (*Vaccinum spp*.) using high-perfomance liquid chromatography/mass spectrometry. *J. Agric. Food Chem.* **2001,** 49, 1270-1276.

6. Maatta, K.R.; Kamal-Eldin, A,; Torronen, R. High-performance liquid chromatography analysis of phenolic compounds in berries with diode array and electrospray ionization mass spectrometric detection: *Ribes* species. *J. Agric. Food Chem.* **2003**, 51, 6736-6744.

7. Maatta-Rihinein, K.R.; Kamal-Eldin, A.; Mattila, P.H.; Gonzales-Paramas, A.M.; Torronen, A.R. Distribution and contents of phenolic compounds in eighteen Scandinavian berry species. *J. Agric. Food Chem.* **2004,** 52, 4477-4486.

8. Mullen, W.; Graf, B.A.; Caldwell, S.T.; Hartley, R.C.; Duthie, G.G.; Edwards, C.A.; Lean, M.E.; Crozier, A. Determination of flavonol metabolites in plasma and tissues of rats by HPLC-radiocounting and tandem mass spectrometry following oral ingestion of [2-^{14}C]quercetin-4'-glucoside. *J. Agric. Food Chem.***2002,** 50, 6902-6909.

9. Mullen, W.; Hartley, R.C.; Crozier, A. Detection and identification of ^{14}C-labelled flavonol metabolites by high-performance liquid chromatography-radiocounting and tandem mass spectrometry. *J. Chromatogr. A,* **2003,** 1007, 21-29.

10. Mullen, W.; Yokota, T.; Lean, M.E.; Crozier, A. Analysis of ellagitannins and conjugates of ellagic acid and quercetin in raspberry fruits by LC-MS^{n}. *Phytochemistry,* **2003,** 64, 617-624.

11. Hong, V.; Wrolstad, R.E. Use of HPLC separation photodiode array detection for characterization of anthocyanins *J. Agric. Food Chem.* **1990,** 38, 708-715.

12. Burns, J.; Yokota, T.; Ashihara, H.; Lean, M.E.; Crozier, A. Plant foods and herbal sources of resveratrol. *J. Agric. Food Chem..* **2002,** 50, 3337-3340.

13. Mullen, W.; McGinn, J.; Lean, M.E.; MacLean, M.R.; Gardner, P.; Duthie, G.G.; Yokota, T.; Crozier, A. Ellagitannins, flavonoids, and other phenolics in red raspberries and their contribution to antioxidant capacity and vasorelaxation properties. *J. Agric. Food Chem,* **2002,** 50, 5191-5196.

14. Rommel, A.; Wrolstad, R. Influence of acid and base hydrolysis on the phenolic composition of red raspberry juice. *J. Agric. Food Chem.* **1993,** 41, 1237-1241.

15. Zafrilla, P.; Federico, F.; Tomas-Barberan, F.A. Effect of processing and storage on the antioxidant ellagic acid derivatives and flavonoids of red raspberry (*Rubus idaeus*) jams. *J. Agric. Food Chem.* **2001,** 49, 3651-3655.

16. Marks, S.C.; Mullen, W.; Crozier, A. Flavonoid and hydroxycinnamate profiles of English apple ciders. *J. Agric. Food Chem.* **2007,** 55, 8723-8730.

17. Schuster, B.; Herrmann, K. Hydroxybenzoic and hydroxycinnamic acid derivatives in soft fruits. *Phytochemistry,* **1985,** 24, 2761-2764.

18. Froytlog, C.; Slimestad, R.; Andersen, O.M. Combination of chromatographic techniques for the preparative isolation of anthocyanins applied on blackcurrant (*Ribes nigrum*) fruits. *J. Chromogr. A,* **1998,** 825, 89-95.

19. Slimestad, R.; Solheim, H. Anthocyanins from blackcurrants (*Ribes nigrum L.*). *J. Agric. Food Chem.* **2002,** 50, 3228-3231.

20. Häkkinen, S.H.; Karenlampi, S.O.; Heinonen, I.M.; Mykkänen,H.M.; Törrönen, AR. Content of the flavonols quercetin, myricetin, and kaempferol in 25 edible berries. *J. Agric. Food Chem.* **1999,** 47, 2274-2279.

21. Justesen, U.; Knisthsen, P.; Leth, T. Quantitative analysis of flavonols, flavones and flavanones in fruits, vegetables and beverages by high-performance liquid chromatography with photo-diode array and mass spectrometic detection. *J. Chromatogr. A,* **1998,** 799, 101-110.

22. Sellapan, S.; Akoh, C.C.; Krewer, G. Phenolic compounds and antioxidant capacity of Georgia-grown blueberries and blackberries. *J. Agric. Food Chem.* **2002,** 50, 2432-2438.

23. Clifford, M.N.; Johnston, K.L.; Knight, S.; Kuhnert, N. Hierarchical scheme for LC-MS^n identification of chlorogenic acids *J. Agric. Food Chem.* **2003,** 51, 2900-2911.

24. Giusti, M.; Rodriguez-Saona, L.E.; Griffin, D.; Wrolstad, R.E. Electrospray and mass spectrometry as tools for anthocyanin analysis. *J. Agric. Food Chem.* **1999,** 47, 4657-4664.

25. Mullen, W.; Stewart, M.; Lean, M.E.J.; Gardner, P.; Duthie, G.G.; Crozier,A. Effect of freezing and storage on the phenolics, ellagitannins, flavonoids and antioxidant capacity of Scottish red raspberries. *J. Agric. Food Chem.* **2002,** 50:, 197-5201

26. Tanaka, T.; Tachibana, H.; Nonaka, G.; Nishioka, I.; Hsu, F.L.; Kohda, H.; Tanaka, O. Tannins and related compounds. CXXII. New dimeric, trimeric and tetrameric ellagitannins, lambertianins A-D, from *Rubus lambertianus* Seringe. *Chem. Pharm. Bull. (Tokyo),* **1993,** 41, 1214-1220.

27. Maatta, K.; Kaml-Eldin, A.; Torronen, R.. Phenolic compounds in berries of black, red, green and white currants (*Ribes sp*.). *Antiox Redox Signal,* **2001,** 3:, 81-993.

28. Oydvin, J. Inheritance of four cyanidin-3-glycosides in red currant. *Hort. Res.* **1974,** 14, 1-7.

29. Vvendenskaya, I.O.; Rosen, R.T.; Guido, J.E.; Russell, D.J.; Mills, K.A.; Vorsa, N. Characterization of flavonols in cranberry (*Vaccinium macrocarpon*) powder. *J. Agric. Food Chem.* **2004,** 52, 188-195.

Table S1. Phenolic compounds identified in blackcurrant by HPLC with diode array and MS^3 detection[a]

Peak	t_R (min)	Compound	λ_{max} (nm)	[M-H] (*m/z*)	MS^2 ions (*m/z*)	MS^3 ion (*m/z*)
1	12.9	caffeic acid-*O*-glucoside	330	341	179 [CafAc] ($[M-H]^-$–Hex)	
2	13.5	delphinidin-3-*O*-galactoside	520	465*	303 [Del] ($[M+H]^+$–Gal)	
3	14.8	delphinidin-3-*O*-glucoside	520	465*	303 [Del] ($[M+H]^+$–Glc)	
4	17.0	delphinidin-3-*O*-rutinoside	520	611*	465 ($[M+H]^+$–Rham), 303 [Del] ($[M+H]^+$–Glc–Rham)	
5	18.3	cyanidin-3-*O*-glucoside	520	449*	287 [Cyan] ($[M+H]^+$–Glc)	
6	20.3	cyanidin-3-*O*-rutinoside	520	595*	449 ($[M+H]^+$–Rham), 287 [Cyan] ($[M+H]^+$–Glc–Rham)	
7	22.4	peonidin-3-*O*-galactoside	520	463*	301 [Peon] ($[M+H]^+$–Gal)	
		petunidin-3-*O*-rutinoside		625*	479 ($[M+H]^+$- Rham), 317 [Pet] ($[M+H]^+$–Rham–Glc)	
8	24.0	malvidin-3-*O*-galactoside	520	493*	331 [Malv] ($[M+H]^+$–Gal)	
		peonidin-3-*O*-glucoside		463*	301 [Peon] ($[M+H]^+$–Glc)	
9	25.9	peonidin-3-*O*-rutinoside	520	609*	463 ($M+H]^+$–Rham), 301 [Peon] ($[M+H]^+$- Glc–Rham)	
10	31.3	myricetin-3-*O*-rutinoside	355	625	317 [Myr] ($[M-H]^-$–Rut)	
11	31.8	myricetin-*O*-glucuronide	355	493	317 [Myr] ($[M-H]^-$–GlcA)	
12	35.0	myricetin-3-*O*-(6''-O-malonyl)glucoside	355	521	317 [Myr] ($[M-H]^-$–Glc–Mal)	
13	37.5	quercetin-3-*O*-rutinoside	350	609	301 [Q] ($[M-H]^-$–Rut)	
14	39.1	quercetin-3-*O*-glucoside	350	463	301 [Q] ($[M-H]^-$–Glc)	271, 255, 179
15	40.5	delphinidin-3-*O*-(6''-*p*-coumaroyl)glucoside	525	611*	303 [Del] ($[M+H]^+$–Coum–Glc)	
16	42.5	quercetin-3-*O*-(6''-O-malonyl)glucoside	350	505	301 [Q] ($[M-H]^-$–Glc–(Mal)	271, 255, 179
17	43.9	kaempferol-3-*O*-rutinoside	315	593	285 [K] ($[M-H]^-$–Rut)	
18	45.2	kaempferol-3-*O*-galactoside	340	477	301 [K] ($[M-H]^-$–Gal)	

[a] CafAc, caffeic acid; Del, delphinidin; Hex, hexose; Gal, galactose; Glc, glucose; Rut, rutinose; Arab, arabinose; Cyan, cyanidin; Pet, petunidin; Peon, peonidin; Malv, malvidin; Myr, myricetin; GlcA, glucuronyl; Pent, pentosyl; Mal, malonyl; Q, quercetin; Coum, coumaroyl; K, kaempferol; t_R, retention time, Peak numbers and retention times refer to HPLC traces in **Figure 1**. * positively charged molecular ion ($[M+H]^+$)

Table S2. Phenolic compounds identified in blueberries by HPLC with diode array and MS^3 detection[a]

Peak	t_R (min)	Compound	λ_{max} (nm)	[M-H] (*m/z*)	MS^2 ions (*m/z*)	MS^3 ions (*m/z*)
1	13.5	delphinidin-3-*O*-galactoside	520	465*	303 [Del] ($[M+H]^+$–Gal)	
2	14.8	delphinidin-3-*O*-glucoside	520	465*	303 [Del] ($[M+H]^+$–Glc)	
3	16.7	cyanidin-3-*O*-galactoside	520	449*	287 [Cyan] ($[M+H]^+$–Gal)	
		delphinidin-3-*O*-arabinoside		435*	303 [Del] ($[M+H]^+$–Arab)	
4	19.4	petunidin-3-*O*-galactoside	520	479*	317 [Pet] ($[M+H]^+$–Gal)	
5	20.2	cyanidin-3-*O*-arabinoside	515	419*	287 [Cyan] ($[M+H]^+$–Arab)	
6	22.4	petunidin-3-*O*-arabinoside	520	449*	317 [Pet] ($[M+H]^+$–Arab)	
		peonidin-3-*O*-galactoside		463*	301 [Peon] ($[M+H]^+$–Gal)	
7	24.0	malvidin-3-*O*-galactoside	520	493*	331 [Malv] ($[M+H]^+$–Gal)	
8	24.7	malvidin-3-*O*-glucoside	525	493*	331 [Malv] ($[M+H]^+$–Glc)	
		delphinidin-3-*O*-(6''-*O*-acetyl)glucoside		507*	303 [Del] ($[M+H]^+$–AcGlc)	
9	25.7	peonidin-3-*O*-arabinoside	525	433*	301 [Peon] ($[M+H]^+$–Arab)	
10	27.4	malvidin-3-*O*-arabinoside	525	463*	331 [Malv] ($[M+H]^+$–Arab)	
11	30.4	petunidin-3-*O*-(6''-*O*-acetyl)glucoside	525	521*	317 [Pet] ($[M+H]^+$–AcGlc)	
12	30.9	myricetin-3-*O*-galactoside	355	479	317 [Myr] ($[M-H]^-$–Gal)	
13	33.8	quercetin-*O*-diglucoside	355	625	301 [Q] ($[M-H]^-$–Glc–Glc)	
		5-*O*-feruloylquinic acid	325	367	191, 179, 135	
14	35.5	malvidin-3-*O*-(6''-*O*-acetyl)glucoside	530	535*	331 [Malv] ($[M+H]^+$–AcGlc)	
15	37.6	quercetin-3-*O*-rutinoside	355	609	301 [Q] ($[M-H]^-$–Rut)	179, 151
16	38.1	quercetin-3-*O*-galactoside	355	463	301 [Q] ($[M-H]^-$–Gal)	
17	39.2	quercetin-3-*O*-glucoside	355	463	301 [Q] ($[M-H]^-$–Glc)	
18	43.0	quercetin-3-*O*-arabinoside	355	433	301 [Q] ($[M-H]^-$–Arab)	271, 255, 179
		quercetin-3-*O*-(6''-*O*-acetyl)glucoside	355	505	301 [Q] ($[M+H]^-$–AcGlc)	

[a] Del, delphinidin; Glc, glucose; Cyan, cyanidin; Arab, arabinose; Pet, petunidin; Peon, peonidin; Malv, malvidin; Gal, galactose; AcGlc, acetylglucose; Myr, myricetin; Hex, hexose; Rut, rutinose; Q, quercetin; Pent, pentose; t_R, retention time. [a] Peak numbers and retention times refer to HPLC traces in **Figure 2.** * positively charged molecular ion ($[M+H]^+$)

Table S3. Phenolic compounds identified in raspberries by HPLC with diode array and MS^3 detection[a].

Peak	t_R (min)	Compound	λ_{max} (nm)	$[M-H]^-$ *(m/z)*	MS^2 ions *(m/z)*	MS^3 ion *(m/z)*
1	16.1	cyanidin-3-*O*-sophoroside	515	611*	287 [Cyan] ($[M+H]^+$–Soph)	
2	18.0	cyanidin-3-(2''-*O*-glucosyl)rutinoside	515	757*	611 ($[M+H]^+$–Rham), 287 [Cyan] ($[M+H]^+$–Rham–Glc–Glc)	
		cyanidin-3-*O*-sambubioside		581*	287 ($[M+H]^+$–Samb)	
		cyanidin-3-*O*-glucoside		449*	287 [Cyan] ($[M+H]^+$–Glc)	
3	18.9	pelargonidin-3-*O*-sophoroside	500	595*	271 [Pel] ($[M+H]^+$–Soph)	
4	20.3	cyanidin-3-*O*-rutinoside	510	595*	449 (M^+-Rham), 287 [Cyan] (M^+–Rham–Glc)	
5	21.2	pelargonidin-3-*O*-glucoside	500	433*	271 [Pel] ($[M+H]^+$–Glc)	
		pelargonidin-3-*O*-(2''-*O*-glucosyl)rutinoside		741*	271 [Pel] ($[M-H]^+$–Rham-Glc–Glc)	
6	29.6	lambertianin C	250	1401[2] (2801)	1869, 1567 (1869–HHDP), 1265 (1869–HHDP–HHDP), 1251, 935 (1869–HHDP–HHDP–Glc–galloyl), 633 (1869–HHDP–HHDP–Glc–galloyl–HHDP)	
7	30.8	sanguiin H-6	250	1869	1567 ($[M-H]^-$–HHDP), 1265 ($[M-H]^-$–HHDP–HHDP), 1235, 933 ($[M-H]^-$–HHDP–HHDP–Glc-galloyl), 631 ($[M-H]^-$–HHDP–HHDP-Glc-galloyl-HHDP)	
8	32.7	ellagic acid-*O*-pentoside	360	433	301 [HHDP] ($[M-H]^-$–pent)	257
9	33.5	ellagic acid-O-pentoside	360	433	301 [HHDP] ($[M-H]^-$–pent)	257
10	34.4	ellagic acid	360	301	257	
11	35.8	quercetin-*O*-galactosylrhamnoside	340	609	301 [Q] ($[M-H]^-$–Gal–Rham)	
12	37.1	quercetin-3-*O*-(2''-*O*-glucosyl)rutinoside	340	609	301 [Q] ($[M-H]^-$–Glc–Rham)	
13	37.7	quercetin-3-*O*-galactoside	340	463	301 [Q] ($[M-H]^-$–Gal)	
14	39.2	quercetin-3-*O*-glucoside	340	463	301 [Q] ($[M-H]^-$–Glc), 179	
15	42.5	ellagic acid-4-*O*-acetylxyloside	360	475	301 [HHDP] ($[M-H]^-$–XylAc)	

[a] Cyan, cyanidin; Pel, pelargonidin; Soph, sophorose; Samb, sambubiose; Q, quercetin; Glc, glucose; Gal, galactose; Rham, rhamnose; Pent, pentose; Xyl, xylose; XylAc, acetylxylose; AraAc, acetylarabinose; HHDP, hexahydroxydiphenoyl; t_R, retention time [a] Peak numbers and retention times refer to HPLC traces in **Figure 3**. * positively charged molecular ion ($[M+H]^+$).

Table S4. Phenolic compounds identified in redcurrants by HPLC with diode array and MS^3 detection[a].

Peak	t_R (min)	Compound	λ_{max} (nm)	$[M-H]^-$ (*m/z*)	MS^2 ions (*m/z*)	MS^3 ions (*m/z*)
1	9.1	4-hydroxy-benzoic acid-*O*-hexoside	260	299	137 [HbenzAc] ($[M-H]^-$–Hex)	
2	12.8	caffeic acid-*O*-glucoside	330	341	179 [CafAc] ($[M-H]^-$–Glc)	
3	18.0	cyanidin-3-*O*-sambubioside	515	581*	287 [Cyan] ($[M+H]^+$–Samb)	
4	20.3	cyanidin-3-*O*-rutinoside	515	595*	449 ($[M+H]^+$–Rham), 287 [Cyan] ($[M+H]^+$-$^-$Glc–Rham)	
		cyanidin-3-*O*-(2''-*O*-xylosyl)rutinoside		727*	581 ($[M+H]^+$–Rham), 287 [Cyan]($[M+H]^+$–Xyl–Rut)	
5	31.1	myricetin-3-*O*-rutinoside	355	625	317 [Myr] ($[M-H]^-$–Rut)	
6	31.6	myricetin-*O*-rhamnoside	330	463	317 [Myr] ($[M-H]^-$–Rham)	
7	37.4	quercetin-3-*O*-rutinoside	355	609	301 [Q] ($[M-H]^-$–Rut),	271, 255, 179
8	38.0	quercetin-3-*O*-galactoside	355	463	301 [Q] ($[M-H]^-$–Gal)	271, 255, 179
9	39.1	quercetin-3-*O*-glucoside	355	463	301 [Q] ($[M-H]^-$–Glc),	271, 255, 179
10	43.0	quercetin-3-*O*-(6''-*O*-malonyl)glucoside	345	505	463 ($[M-H]^-$–Rut), 301 [Q] ($[M-H]^-$–Hex-–Mal), 179	
11	43.6	kaempferol-*O*-rutinoside	345	593	285 [K] ($[M-H]^-$–Rut)	
12	45.2	kaempferol-3-*O*-galactoside	340	447	285[K] ($[M-H]^-$–Gal)	
13	45.9	kaempferol-3-*O*-glucoside	340	447	285[K] ($[M-H]^-$–Glc)	

[a] HbenzAc, 4-hydroxybenxoic acid; Hex, hexose; CafAc, Caffeic acid; Cyan, cyanidin; Samb, sambubiose; Rut, rutinose; Xyl, xylose; Myr, Myricetin; Rham, rhamnose; Q, quercetin; Glc, glucose; Mal, malonic acid; K, kaempferol; t_R, retention time. Peak numbers and retention times refer to HPLC traces in **Figure 4**. * positively charged molecular ion - $[M+H]^+$.

Table S5. Phenolic compounds identified in cranberries by HPLC with diode array and MS^3 detection[a].

Peak	t_R (min)	Compound	λ_{max} (nm)	[M-H] (*m/z*)	MS^2 ions (*m/z*)	MS^3 ion (*m/z*)
1	13.1	procyanidin dimer	290	577	425, 289 [Cat] ($[M-H]^-$–Cat)	
2	16.8	cyanidin-3-*O* -galactoside	515	449*	287 [Cyan] ($[M+H]^+$–Gal)	
3	18.4	*p*-coumaric acid-*O*-hexoside		325	163 [CoumAc] ($[M-H]^-$–Hex),145,187	
4	20.3	cyanidin-3-*O*-arabinoside	515	419*	287 [Cyan] ($[M+H]^+$–Arab)	
5	21.7	(–)-epicatechin	280	289	245	
6	22.4	peonidin-3-*O*-galactoside	515	463*	301 [Peon] ($[M+H]^+$–Gal)	
7	24.2	peonidin-3-*O*-glucoside	515	463*	301 [Peon] ($[M+H]^+$–Glc)	
8	25.7	peonidin-*O*-arabinoside	515	433*	301 [Peon] ($[M+H]^+$–Arab)	
9	27.4	malvidin-3-*O*-arabinoside	520	463*	331 [Malv] ($[M+H]^+$–Arab)	
10	30.9	myricetin-3-*O*-galactoside	355	479	317 [Myr] ($[M-H]^-$–Gal)	271, 179, 151
11	32.7	procyanidin dimer	280	577	425, 289 [Cat] ($[M-H]^-$–Cat)	
12	35.8	myricetin-3-*O*-arabinoside	355	449	317 [Myr] ($[M-H]^-$–Arab)	271, 179, 151
13	37.7	procyanidin dimer	280	577	425, 289 [Cat] ($[M-H]^-$–Cat)	
14	38.2	quercetin-3-*O*-galactoside	355	463	301 [Q] ($[M-H]^-$–Gal)	271, 255, 179
15	41.4	quercetin-3-*O*-(2''-O-xylosyl)pyranoside	355	433	301 [Q] ($[M-H]^-$–Xyl)	271,255,179
16	43.2	quercetin-3-*O*-arabinosylpyranoside	350	433	301 [Q] ($[M-H]^-$–Arab)	
17	43.8	quercetin-3-*O*-arabinosylfuranoside	350	433	301 [Q] ($[M-H]^-$–Arab)	271,255,179
18	46.1	quercetin-3-*O*-rhamnoside	345	447	301 [Q] ($[M-H]^-$–Rham)	271,255,179

[a] Cat, (epi)catechin; CafAc, caffeic acid; CoumAc, *p*-coumaric acid; Cyan, cyanidin; Mal, malvidin; Peon, peonidin; Myr, myricetin; Q, quercetin; Arab, arabinose; Glc, glucose; Gal, galactose; Rham, rhamnose; Pent, pentose; Hex, hexose; t_R, retention time. Peak numbers and retention times refer to HPLC traces in **Figure 5**. * positively charged molecular ion ($[M+H]^+$)