

Title Flavonol content and antioxidant capacity of various blackberry and blueberry genotypes determined by high-performance liquid chromatography/ mass spectrometry

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Abstract

Blueberries and blackberries are known to contain appreciable levels of flavonoids that may provide health benefits as dietary antioxidants. Although anthocyanins have been well characterized in berries, little information exists on the composition and content of flavonol glycosides in the fruit. The objective was to establish an HPLC method coupled with photodiode array and mass spectrometric detection that could be used to effectively separate, identify and quantify flavonol glycosides in blueberry and blackberry genotypes. The antioxidant capacities of fractionated flavonol extracts were also determined. Quantification of individual flavonols in berry extracts (60:3:37; methanol-formic acid-water) was achieved by HPLC with UV/VIS diode-array detection, using an Aqua C18 column. Electrospray mass-spectroscopy was used for identification. Flavonols were fractionated by HPLC and their antioxidant capacities determined by the oxygen radical absorbing capacity (ORAC) assay and Photochem antioxidant analyzer, respectively. Seven flavonols of quercetin-sugar conjugates were identified in Kiowa blackberry including: rutinoid; galactosid; glucosid; xylosid; [6²(3-hydroxy-3-methylglutaroyl)]-b-galactosid; glucosylpentosid; oxalylpentosid. Twelve flavonols were detected in Ozarkblue blueberry. Of these, myricetin 3-hexosid and eight quercetin-sugar conjugates including: rutinoid; galactosid; glucosid; pentosid; glucosylpentosid; oxalylpentosid; rhamnosid; and acetylhexosid, were identified. In Bluecrop blueberry, two additional quercetin-sugar conjugate were identified: glucuronid and caffeoylhexosid. Quercetin glycosides accounted for >75% of total flavonols in the blueberry genotypes. Total flavonol contents ranged from 9.9-15.0 mg/100 mg for blackberries and 19.2-32.0 mg/100 mg for blueberries. Inhibition of peroxy and superoxide anion radicals by the flavonol fractions ranged from 1.03-1.54 mmol TE/ mg and 0.47-0.62 mmol TE/mg for blackberries and 0.51-1.21 mmol TE/mg and 0.39-0.56 mmol TE/mg for blueberries, respectively. The HPLC method allowed for complete separation and identification of flavonols commonly found in blackberries, and blueberries. Our results showed that blueberry and blackberry genotypes varied significantly in flavonol content and antioxidant capacity, but flavonol content did not correlate well with antioxidant capacity.