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Original Article

# Flavonoids from black chokeberries, *Aronia melanocarpa*

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**Abstract**

Black chokeberry, *Aronia melanocarpa* (Michx.) Elliott (Rosaceae), was investigated for its flavonoid content. The flavanone eriodictyol 7-*O*-*β*-glucuronide (**1**) together with the quercetin derivatives 3-*O*-(6″-*O*-*β*-arabinosyl-*β*-glucoside) (**2**), 3-*O*-(6″-α-rhamnosyl-*β*-galactoside) (**3**), 3-*O*-(6″-α-rhamnosyl-*β*-glucoside) (**4**), 3-*O*-*β*-galactoside (**5**) and 3-*O*-*β*-glucoside (**6**), were detected in the fruits and flower umbels. The rare compounds **1**–**3** were isolated and structurally elucidated by use of 1D- and 2D-nuclear magnetic resonance experiments together with electrospray mass spectrometry. Compounds **4**–**6** were characterized by co-chromatography and by liquid chromatography-mass spectrometry. The black chokeberries contained >71 mg flavonols per 100 g fresh weight.


*Keywords:* Black chokeberries; *Aronia melanocarpa*; Rosaceae; Flavanone; Flavonols

## 1. Introduction

Black chokeberries, *Aronia melanocarpa* (Michx.) Elliott, belongs to the Rosaceae family, and is a natural shrub in Northern America (Strigl et al., 1995; Jeppsson, 1999). The dark berries, which are similar to blackcurrants with respect to size and color, have been used by native Americans (Abnakians and Potawatomians) both as a food resource and in traditional medicine for treatment of cold (Rousseau, 1947; Smith, 1933). In recent years black chokeberries have been highlighted with respect to its potential use as a food colorant (Bridle and Timberlake, 1997) and

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as a source for valued phytonutrients. The anthocyanin level of the berries has been reported to be as high as 1% on a dry weight basis (Strigl et al., 1995), whereas the total phenolic content has been reported to be more than 20 mg/g (gallic acid equivalents) (Kahkonen et al., 1999). Four anthocyanins are responsible for the dark red color of these fruits: 3-*O*-galactoside, 3-*O*-glucoside, 3-*O*-arabinoside and 3-*O*-xyloside of cyanidin (Oszmianski and Sapis, 1988; Strigl et al., 1995). Chlorogenic and neochlorogenic acids are dominant among the aromatic acids (Slimestad et al., 2002). The high content of phenolics seems to correlate with the antioxidant activity reported for these berries (Kahkonen et al., 1999; Gasiorowski et al., 1997).

Besides the anthocyanins content, HPLC chromatograms reveal that the berries contain several compounds that are supposed to be flavonols. With the exception of quercetin aglycone which has been liberated upon acidic hydrolysis of berries extract (Häkkinen et al., 1999), other flavonol structures presented here have not been reported from this species. However, other berries within the Rosaceae family have been reported to contain derivatives of kaempferol and quercetin such as kaempferol 3-glucoside-7-xyloside and quercetin 3-[6″-(3-hydroxy-3-methyl-glutaryl) galactoside in *Rubus* species, and the 3-gentiobiosides of both kaempferol and quercetin in *Sorbus pendula* (Harborne and Baxter, 1999).

This work describes the structures of five flavonols that have been isolated from flower umbels of *A. melanocarpa* and also detected by chromatography in the berries of the same plant. The flowers were found to be a better source for isolation of these structures. Also the structure of a flavanone from the extract of the berries is described. In addition the amount of the different anthocyanins, chlorogenic acids and flavonols present was analyzed.

## 2. Materials and methods

### 2.1. Sample preparation

Three kinds of samples were prepared: (i) extract of berries for the isolation of a flavanone; (ii) a set of berries extracts for HPLC analysis of flavonoids and chlorogenic acids; and finally (iii) a flower umbels extract for the isolation of the flavonols that also occurred in the berries.

(i) Fruits of black chokeberries were collected in the middle of August 2001 at Sola, Norway, and immediately stored at −10°C. About 20 kg berries was extracted with 0.1% hydrochloric acid in 40 l methanol for 48 h and concentrated in vacuo to a small volume (about 5 L). To this was added 0.2 L of water, and the abstract was partitioned three times against equal volumes of ethyl acetate. The combined ethyl acetate fractions was concentrated and finally purified on Amberlite XAD-7 according to an established procedure (Andersen, 1988).

(ii) HPLC analysis was performed on four samples of 50 g frozen berries each. They were each extracted with 5 × 200 mL methanol (0.1% HCl, v/v for 6 h and the extracts were combined. Aliquots of 20 μL of these extracts were directly injected into the HPLC-instrument.

(iii) Flower umbels of black chokeberries were collected on May 2, 2001 at Sola, Norway, and stored in the dark at −10°C until extraction. A 74.9 g fresh weight samples of the umbels was extracted with 500 mL methanol (0.1% v/v of trifluoroacetic acid—TFA) for 24 h at ambient temperature. The extract was concentrated in vacuo, and about 50 mL water was added