

***Aronia melanocarpa* – the Styrian ‘super berry’: A flavour characterisation of black chokeberry juice**

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Abstract

The juice of black chokeberries (*Aronia melanocarpa*) was in the focus of this investigation. Whereas there are several studies available about the health beneficial effects of aronia products, which are mainly based on the extraordinary high polyphenol concentrations, little is known about the flavour properties of aronia products. The volatile compounds of aronia juices were investigated by one- and two-dimensional gas chromatographic methods. In addition, gas chromatography-olfactometry as well as sensory evaluation was applied to explore the sensory properties of compounds and juices, respectively. The results show an interesting composition of the flavour compounds that is dominated by alcohols, aldehydes, free fatty acids, terpenes, norisoprenoids and cinnamic acid metabolites. Most striking is the lack of fruit esters in aronia juices when compared with volatiles from other fruit and berry juices, leading to very weak fruity notes in the aronia products. These results serve as a basis for future investigations on the technological impact on flavour formation during the production of aronia juices.

Introduction

The black chokeberry (*Aronia melanocarpa*) is a shrub that has traditionally been cultivated in Eastern European countries as well as in North America where it has also been used as domestic remedy. Recently, the black chokeberry has been included into the group of ‘superfoods’ which made this berry type popular. In Southern Austrian regions, the crop area for the cultivation of aronia has increased drastically within the last few years with the aim to produce a domestic superfood. Its superfood status is mainly based on the very high antioxidative capacities due to exceptionally high concentrations of polyphenols (i.e. anthocyanins and proanthocyanins, flavonols as well as phenolic acids) [1]. Furthermore, the black chokeberry is rich in minerals and trace elements as well as some vitamins [2]. Several studies proved the health benefits of aronia showing positive impact on blood pressure values, cholesterol- and triglyceride concentrations, anti-inflammatory effects, anti-tumor activity as well as the exhibition of immunomodulatory activity in breast cancer patients [2, 3].

Due to the high concentrations of anthocyanins, and as a consequence the extraordinary colour intensity, aronia products (e.g. extracts, concentrates or dried products) have been of interest for food industry as a natural food colourant. Only recently, the consumption of aronia products as health promoting food has become popular. Austrian farmers founded a consortium named ‘Aronia Austria’ to promote NFC (not from concentrate) aronia juice as a domestic superfood. However, in contrast to other juices and nectars from domestic fruits, the flavour characteristics of high quality aronia juice are not well described. As a consequence, we investigated aronia juice produced from Austrian aronia berries with emphasis on volatile compounds and sensory properties.

Experimental

Material

Aronia juices were prepared from Styrian aronia berries (variety Nero) from the harvest 2015 by a small local fruit processing company. All investigated juices were NFC juices. The juices were prepared after enzymatic treatment and were pressed using a belt press. All juices were stored in glass bottles in the dark at 5°C until further use. Only juices that were awarded with at least 18 out of 20 points at a local juice tasting competition prior to this study were included in these investigations.

Sensory evaluation

Sensory evaluation of the juices was performed by an expert panel (14 well-trained panellists) under standardised conditions. All panellists had vast sensory experience with fruit products and achieved specific training on aronia products prior to this study. Descriptive analyses to select appropriate attributes for the products as well as quantitative descriptive analyses (QDA[®]) were applied. Sensory data were recorded using Compusense sensory software (Compusense Inc., Guelph, Canada).

Analysis of the volatile compounds

Enrichment of the volatile compounds was performed by headspace solid phase microextraction (HS-SPME; 60°C, 20 min, 50/30 µm DVB/CAR/PDMS fibre, 2 cm stable flex fibre) for all types of GC-analyses. 200 µL of aronia juice with the addition of 50 mg NaCl were transferred into 20 mL headspace vials. 2-Octanol (100 ng absolute) was added as internal standard. Four replicates of each sample were prepared and analysed. 1-dimensional GC-MS analysis was performed on Agilent GC 7890, MS 5975c VL MSD, Santa Clara, CA, USA; HP5 30 m*0.25 mm*1 µm, EI (70eV), scan range 35-350 amu. Comprehensive GC x GC-MS was carried out on Shimadzu GC-2010 Plus coupled with Shimadzu GCMS-QP2010 Ultra, Shimadzu Europa GmbH; 1st dim.: ZB-5MS 30 m *0.25 mm*0.25 µm and 2nd dim.: BPX50 2.5 m *0.15 mm*0.15 µm, Zoex cryo modulator, 5s modulation frequency, Hot Jet 280°C, 350 msec pulse time; EI (70 eV). Identification of the compounds was based on the comparison of the obtained mass spectra to those from MS libraries or authentic reference compounds as well as on retention indices (RI). Linear-temperature programmed RI were calculated using n-alkanes (C₅-C₂₆) and compared to data from authentic reference compounds and data from literature. For comprehensive GC x GC-MS, RI were calculated for the 1st dimension.

For GC olfactometry, 1 mL of aronia juice with the addition of 500 mg NaCl was used. GCO/GC-FID analysis was performed on a non-polar column (Hewlett Packard 5890 series II equipped with an FID and a Gerstel Olfactory Detection Port; Split ratio FID:ODP 1:1; analytical column DB5, 30 m*0.32 mm*0.25 µm; splitless injection). Detection frequency (DF) with the use of 5 trained panellists was performed to determine the odour active compounds with the potentially highest sensory impact. Each GCO run was performed in duplicate resulting in a total of 10 GCO runs for DF analysis. Identification of the odour active compounds was performed by the determination of linear temperature programmed RI and the odour descriptors given for the odour impressions from authentic reference compounds or literature.

Statistical evaluation of the results

Principal component analysis (PCA) using a Pearson correlation matrix was performed to correlate concentrations of volatile compounds from 15 different aronia

juices with results from QDA[®]. PCA was performed with XLSTAT Sensory by Addinsoft (France).

Results and discussion

Due to its pronounced antioxidative properties, the consumption of aronia juice has gained increasing popularity on the (local) market. However, little is known about the sensory properties and the composition of flavour compounds of aronia juice. In this study, we therefore aimed for a basic characterisation of aronia juice volatiles.

In comparison to other juices, aronia juice is somehow different as the products do not show dominant fruitiness. Depending on the juice, astringency and bitterness on the one hand, and woody, balsamic, green and sweaty notes on the other hand significantly influence aronia juice flavour. Figure 1 shows a typical chromatogram (comprehensive GC x GC-MS) of a high quality aronia juice. Several hundred volatile compounds could be detected, 50 thereof were identified. These results show that the volatiles count to the chemical classes of alcohols, aldehydes and ketones, (methyl-branched) short-chain fatty acids, terpenoid compounds and norisoprenoids. In addition, several aromatic compounds as polyphenol degradation products (formed most likely via the shikimic acid pathway and degradation of cinnamic acid, respectively) were identified. The enormous concentrations of 5,6-dihydro-2H-pyran-2-one (up to 1.250 µg/L) have to be pointed out. However, with an odour threshold of higher than 100 mg/L (in water), this compound is not considered to be of relevance for aronia juice flavour. Noticeable is the lack of the typical fruit esters which is most likely the reason for the lack of the fruity notes in the juice. Ethyl-2 (3)-methyl butanoate was identified in the GCO experiment as the only pronounced fruity odour with medium impact and is thus supposed to be responsible for the moderate fruity attributes of the products.

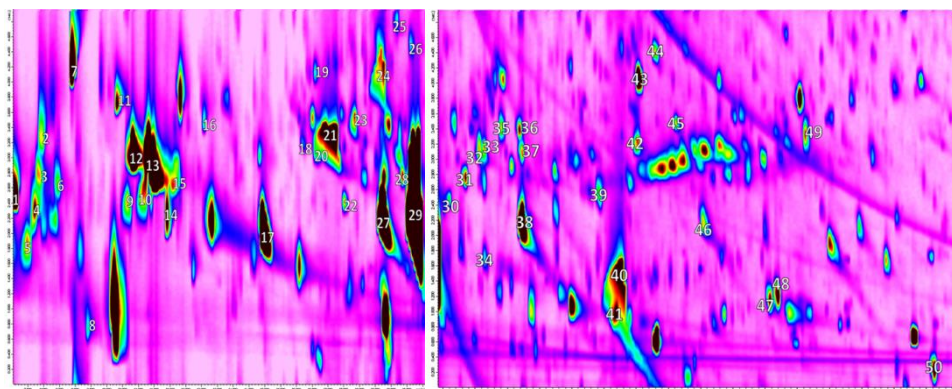


Figure 1: Chromatogram from comprehensive GC x GC-MS of a selected aronia juice (divided into 2 parts); retentions times in x-axis are given in minutes and in y-axis in seconds; 1: (*E*)-3-penten-2-one, 2: 2,3-butanediol, 3: acetylacetone, 4: (*Z*)-2-penten-1-ol, 5: 2-methylpropanoic acid, 6: hexanal, 7: 4-hydroxy-2-pentanone, 8: furfural, 9: 2-methylbutanoic acid, 10: 3-methylbutanoic acid, 11: (*E*)-2-hexenal, 12: (*Z*)-3-hexen-1-ol, 13: (*E*)-2-hexen-1-ol, 14: γ -butyrolactone, 15: 1-hexanol, 16: heptanal, 17: benzaldehyde, 18: 1-heptanol, 19: 6-methyl-5-hepten-2-one, 20: 1-octen-3-ol, 21: hexanoic acid, 22: β -myrcene, 23: (*E*)-3-hexenoic acid, 24: 2-hexenoic acid, 25: sorbic acid, 26: hexyl-2-methyl-2-propenoate, 27: benzyl alcohol, 28: limonene, 29: 5,6-dihydro-2H-pyran-2-one, 30: β -ocimene, 31: γ -terpinene, 32: cis-linalool oxide (furanoid), 33: heptanoic acid, 34: guaiacol, 35: trans-linalool oxide (furanoid), 36: nonanal, 37: linalool, 38: 2-phenylethanol, 39: 1-phenyl-1,2-propanedione, 40: benzoic acid, 41: ethyl benzoate, 42: octanoic acid, 43: terpinen-4-ol, 44: α -terpineol, 45: decanal, 46: 3-phenylpropanol, 47: 4-ethylguaiacol, 48: 2,3,6-trimethylphenol, 49: acetovanillone, 50: β -damascenone

Figure 2 shows the results from PCA of 20 aronia volatiles of 15 investigated aronia juices. The selection of the compounds was based on the results from GCO. Products that can be found in quadrants I and IV are described to possess well-balanced odour with slight fruity notes. Unfortunately, the concentrations of ethyl-2(3)-methyl butanoate were too low for quantification and could, thus, not be included in the PCA. Interestingly, volatiles like benzaldehyde, benzyl alcohol or 2-phenylethanol or ethylbenzoate are important for these products and obviously contribute positively to the overall flavour with their balsamic, woody, slightly floral attributes. These volatile also showed high impact in the GCO experiments. Juices with high concentrations of hexanal, (Z)-3-hexen-1-ol and hexanoic acid (quadrant II) were perceived as mainly imbalanced and dominated by green notes, lacking any fruity and berry like odour.

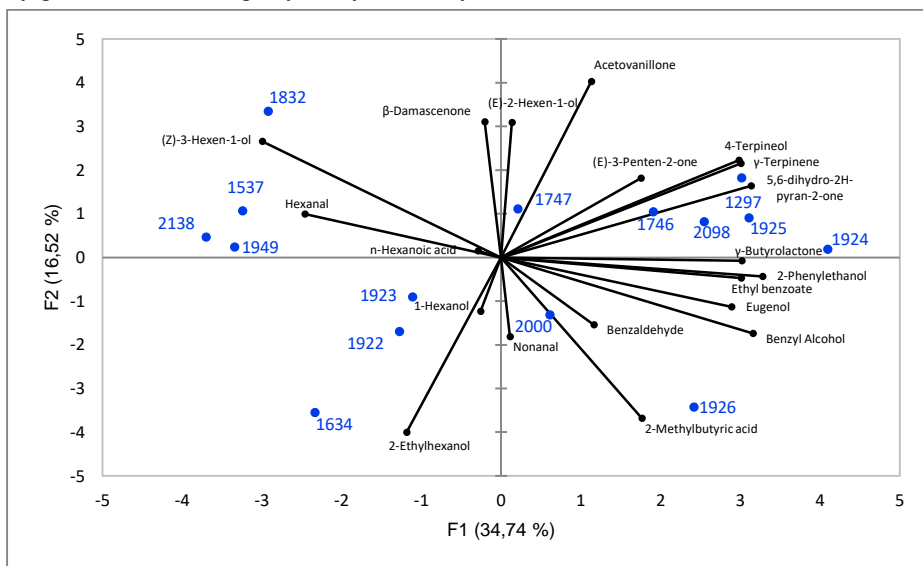


Figure 2: PCA based on the relative concentrations to the internal standard of 20 volatile compounds [$\mu\text{g/L}$] for 15 investigated aronia juices; four digit numbers are sample codes.

The results of this study demonstrate that the flavour of black chokeberry (*Aronia melanocarpa*) juice differs significantly from the juices of other fruits and berries, mainly due to the lack of esters with fruity notes. However, these results serve as a good basis for future investigations of the technological impact on the flavour formation in aronia juices.

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