ORIGINAL PAPER

# Influence of volatile compounds on flavour of selected cultivars of gooseberry

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Abstract The flavour of seventeen red, yellow and green varieties of gooseberry (Ribes grossularia L.) was investigated in this study during two consequent years (2014–2015). Taste, odour, flavour descriptors (sweet, acid/sour, astringent) and off-flavour, together with appearance, colour, texture (firmness, crispiness) and overall acceptability were evaluated sensorially using line scale. Related volatile compounds were assessed by solidphase microextraction coupled to gas chromatography– mass spectrometry. The significant differences ( $p < 0.05$ ) in volatile compounds as well as in sensory properties were found between varieties. The differences between production years were small or not significant. Sensorially no obvious preference was found between red, yellow and/or green varieties. Red 'Karat' and yellow 'Darek' were considered to be the most acceptable with well evaluated all sensory properties. In total, 52 volatile compounds were identified in samples: 19 alcohols, 12 aldehydes, 8 ketones, 11 esters and 2 acids with quantitatively predominating alcohols and acids. (Z)-3-hexen-1-ol, (Z)-3-hexenal, heptan-2-one, methyl butanoate, ethyl butanoate, methyl acetate, ethyl acetate, ethanol and ethanal (with odour activity values  $>1$ ) are considered to contribute to flavour/ acceptability of gooseberry samples.

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# Introduction

Gooseberries (Ribes grossularia L.) are berry-bearing deciduous shrubs, belonging to the genus Ribes L. Fruits are round, oval or pear shaped berries, with smooth or hairy skin, small to large sized (max about 2 cm) (Girard and Sinha [2006](#page-12-0)). Colour varies widely, fruits may be green, white, yellow, or shades of red from pink to purple to almost black. Their flavour is characteristic, mildly astringent, sweet and/or acidic (Harb and Streif [2004\)](#page-12-0); size and shape, colour, firmness, taste and aroma of fruits depend mainly on variety and degree of maturity. Gooseberry fruits are rich in fibre, vitamins (C, E, B complex), minerals and many other nutritious components (flavonoids, phenolic acids, anthocyanins and tannins) (Heiberg and Maage [2003](#page-12-0)), albeit scarce information is available about compositional data on gooseberries (Maage [2002](#page-13-0)). Most of studies published deals with the measuring of phenolic compounds and antioxidant activity, e.g., Filipiak-Szok et al. [\(2012](#page-12-0)) and Chiang et al. ([2013\)](#page-12-0).

Although gooseberries are still considered a minor berry fruit, there is increasing interest of growers, processors and consumers, owing to their natural antioxidant activity (Kaplanova et al. [2016\)](#page-13-0). Both immature (for preservation) and ripe (for direct consumption) gooseberries are practically used. Green gooseberries are firm and tart; they are used for production of wide range of various processed products, such as compotes, jams, juices, wines, liqueurs and/or vinegar; when fully mature, they are soft and several cultivars quite sweet (Harb and Streif [2004;](#page-12-0) Girard and



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Sinha [2006](#page-12-0)). So the practical use depends significantly on sensory quality. Ideally, fruit for direct consumption should be firm, bright, large, with the proper cultivar-specific colour, and free of decay, mechanical or insect injury. A long shelf-life with retention of both firmness and flavour is also desirable for the fruit market (Harb and Streif [2004](#page-12-0); Girard and Sinha [2006](#page-12-0)).

This work is focused on aroma compounds, i.e., volatile compounds contributing to taste and aroma (flavour); most of them arise during fruit ripening (Harb and Streif [2004](#page-12-0)). The composition of aroma compounds of gooseberries and their contribution to aroma have not been comprehensively described so far; only Hempfling et al. [\(2013](#page-12-0)) and Nikfardjam et al. ([2013\)](#page-13-0) published recently results of volatile compounds in several gooseberry varieties, where they identified 122 and 27 volatiles, respectively. (Z)-3-hexenal,  $(E)$ -2-hexenal and methyl butanoate quantitatively predominated; other compounds occurred in relatively low concentrations. The above-mentioned aldehydes and esters, especially butanoates with predominating methyl esters, were considered to be characteristic for volatile profile of gooseberry (Hempfling et al. [2013](#page-12-0)), Nikfardjam et al. [\(2013](#page-13-0)) also identified (Z)-3-hexenal and ethyl acetate as responsible for gooseberry aroma. Harb and Streif ([2004\)](#page-12-0) evaluated sensory quality and acceptability of gooseberries depending on storage conditions. Firmness, sweetness/ acidity balance and possible off-flavour were identified as the determining criteria of sensory quality of gooseberries.

Characterization of aroma profile of a fruits is now of great importance, since it enables to optimize and/or improve the quality of products. The objectives of the present study were (1) to identify and quantify volatile constituents in several varieties of gooseberry, (2) to evaluate flavour using sensory analysis, (3) to demonstrate the differences among samples, and (4) to investigate the contributions of compounds to the sensory quality and overall acceptability of samples. Volatile compounds were extracted by solid-phase microextraction (SPME), identified by gas chromatography–mass spectrometry (GC–MS) and quantified using gas chromatography with flame ionization detector (GC-FID). The descriptive sensory profiling was used for sensory analyses.

#### Experimental

## Chemicals

All chemicals used as reference standards (listed in chapter Results and discussion) were of analytical grade purity; pentanal, hexanal, heptanal, (Z)-2-octenal, nonan-2-one, undecan-2-one, phenylacetaldehyde, benzaldehyde, 3-methylbutan-1-ol, (Z)-3-hexen-1-ol, and 1-octen-3-ol (Sigma-Aldrich, St. Louis, USA), and the remaining compounds were from Merck (Darmstadt, Germany).

## Gooseberry samples

In total, 17 gooseberry varieties were analysed; 8 redfruiting: 'Alan' (Al), 'Hinnonmaki Rot' (HR), 'Karat' (Kar), 'Karmen' (Ka), 'Krasnoslawjanskij' (Kr), 'Remarka' (Re), 'Rolonda' (Rol), 'Tamara' (Ta); 6 yellowfruiting: 'Citronovy obři' (CO), 'Darek' (Da), 'Invicta' (In), 'Rodnik' (Rod), 'Zlaty fik' (ZF), 'Zebin' (Ze); 3 green-fruiting: 'Mucurines' (Mu), 'Prima' (Pr), 'Rixanta' (Rix). The varieties were grown in Research and Breeding Institute of Pomology Ltd. (Holovousy, Czech Republic).

The varieties were grown in the experimental orchard of the Research and Breeding Institute of Pomology Ltd., Holovousy. It has clay soil; the exact location of the orchard is: latitude 50°22'29", longitude 15°34'38", altitude 320 m. The mean temperature and precipitation in this area were 11.41 °C and 607 mm for 2014, while 11.28 °C and 569 mm for 2015, respectively.

The berries were handpicked in their full ripeness (evaluated based on colour and firm texture), during the seasons 2014–2015, immediately stored in the refrigerator at  $5^{\circ}$ C and sensorially evaluated fresh within 2 days; all chemical analyses were performed within 7 days.

#### SPME-GC-FID/MS conditions

For analysis, 1 g of manually homogenized berries was placed into vial for SPME extraction; three samples of every cultivar were taken; every sample was analysed three times (number of repetitions,  $n = 9$ ).

SPME extractions were carried out using Carboxen/ Poly(dimethylsiloxane) (CAR/PDMS) fibre 85 µm (Supelco, Bellefonte, Pensylvania, USA) under the following conditions: extraction temperature  $35^{\circ}$ C; equilibrium time 30 min; extraction time 20 min; desorption temperature 250  $^{\circ}$ C; desorption time 10 min.

Gas chromatograph TRACE GC (ThermoQuest, Milan, Italy) with capillary column DB-WAX (30 m  $\times$  0.32 mm  $\times$  0.5 µm; J. & W. Scientific, Santa Clara, California, USA) was used for GC-FID analyses under the following conditions: injector temperature 250 °C; split-less desorption 5 min; carrier gas  $N_2$ , flow rate  $0.9$  mL min<sup>-1</sup>; flame ionization detector, temperature 220 °C; H<sub>2</sub> inlet 35 mL min<sup>-1</sup>; air inlet 350 mL min<sup>-1</sup>; make up  $N_2$  30 mL min<sup>-1</sup>. The oven ramp temperature was 40  $\degree$ C for 1 min, then it was increased up to 200  $\degree$ C at a rate of 5  $^{\circ}$ C min<sup>-1</sup> and maintained at 200  $^{\circ}$ C for 7 min.

GC–MS analyses were performed on a gas chromatograph HP 6890 with an MS detector 5973 N and the Mass Spectral Library NIST 98 (Agilent, Santa Clara, California, USA); capillary column ZB-5Sil MS (30 m  $\times$  0.25 mm  $\times$  0.25 µm; Phenomenex, Torrance, California, USA) was used with carrier gas He 0.9 mL min<sup>-1</sup> and the oven temperature 50–250 °C at  $3^{\circ}$ C min<sup>-1</sup>. Other GC conditions were the same as described above. MS was operated in electron ionization (EI) mode at 70 eV with a scan range of m/z from 30 to 370.

The standard addition method was used for quantification of analytes to control the influence of the sample matrix. The standards were divided into groups consisting of five chemicals; these standard mixtures were gradually added directly into the sample and analysed in the same manner as the samples. Five content levels, in the range of 0.001–70 mg  $kg^{-1}$  (different for various standards, according to their content in the samples), for ethanol in the range of 0.01–220 mg  $kg^{-1}$  (due to its high content in the samples), were used to establish the calibration curves. Validation and the validation parameters of the used method were identical as previously described by Vitova et al. [\(2013](#page-13-0), [2015\)](#page-13-0). The repeatability was verified by repeated extractions  $(n = 5)$  of the above-mentioned standard mixtures (relative standard deviations \10%), detection and quantification limits were in the range of  $0.001 - 0.50$  mg kg<sup>-1</sup>. Linearity was tested within the range of 0–220 mg  $kg^{-1}$ ; correlation coefficients were all above 0.99.

#### Sensory analyses

The test panel consisted of 22 persons in both years (16 women and 6 men), selected from students and staff of the Department of Food Chemistry and Biotechnology, who were trained (including sensory profiling) for 3 months.

About 20 g of the samples was served in 50 ml glass covered containers, marked with 4-digit codes, in random order. Fresh water was provided to rinse mouth between samples.

The sensory attributes were evaluated using unstructured 100 mm line scale (0–100%), anchored from each end to identify the direction. The list of attributes comprised appearance, taste, odour and texture (ranging from unacceptable to excellent), colour (from atypical to typical, characteristic for red/yellow/green variety), three flavour characteristics (sweet, acid/sour, astringent, from weak to very strong), off-flavour (from imperceptible to very strong), two mouthfeel attributes encompassing firmness (from soft to firm) and crispiness (not crispy to very crispy), and overall acceptability (from unacceptable to delicious). These descriptors were determined in preliminary evaluations by panel of 3 experts (ISO 13299:2016), inspired by Harb and Streif [\(2004](#page-12-0)). Assessors were also asked to add comments for description of possible offflavour.

#### Statistical evaluation

The results of instrumental analyses were treated using parametric one-way analysis of variance (ANOVA) followed by Duncan's test; they are expressed as mean  $\pm$  standard deviation ( $n = 9$ ). The results of sensory analyses were statistically evaluated by means of Kruskal–Wallis test followed by Nemenyi multiple comparison test; they are expressed as mean  $\pm$  standard deviation (number of assessors  $n = 22$ ).

Due to high number of experimental characteristics, the entire experimental dataset was processed by principal component analysis (PCA) to confirm differences among samples. A probability value of  $p \leq 0.05$  was accepted for statistically significantly different results. All analyses were performed using Microsoft Excel 2010 (Microsoft, Redmond, Washington, USA) and Statistica 12 (StatSoft, Tulsa, Oklahoma, USA).

## Results and discussion

## SPME-GC-FID/MS assessment of volatile compounds

It is generally known that the content of volatiles and their contribution to flavour is an important characteristic of fruits (Girard and Sinha [2006](#page-12-0)). However, only two above, mentioned works (Hempfling et al. [2013;](#page-12-0) Nikfardjam et al. [2013](#page-13-0)) deal with the problematic of the volatiles in gooseberries. The main intention of this work was to identify and quantify volatiles in selected red/yellow/green gooseberry varieties grown in two consequent years (2014–2015), to compare their volatile profiles as well as the sensory characteristics and try to investigate which compounds could influence flavour. Simple and fast SPME as alternative to other long-lasting and/or expensive extraction methods was applied for assessment of volatile compounds; it has been previously successfully used by many authors to measure the volatiles of various foods (e.g., Serrano et al. [2009;](#page-13-0) Antalick et al. [2010](#page-12-0); Panighel and Flamini [2014](#page-13-0)). Its limitations in quantification ability were mastered by in-depth quantifying process and keeping constant as many experimental conditions as possible.

In total, 52 volatile compounds were identified and quantified in gooseberry samples in this study; among them 19 alcohols: benzylalcohol, ethanol, propan-1-ol, propan-2 ol, butan-1-ol, butan-2-ol, pentan-1-ol, pentan-2-ol, hexan-1-ol, heptan-1-ol, heptan-2-ol, octan-1-ol, octan-2-ol, nonan-2-ol, decan-1-ol, (Z)-3-hexen-1-ol, 2-methylpropan-1-ol, 3-methylbutan-1-ol, 1-octen-3-ol; 12 aldehydes: phenylacetaldehyde, benzaldehyde, ethanal, propanal, pentanal, hexanal, heptanal, octanal, nonanal, (E)-2Fig. 1 Chromatograms of volatile compounds identified in two selected cultivars; a 'Karat'—red-fruiting; b 'Darek'—yellow-fruiting. Peak numbering: 1 ethanal, 2 propan-2-one, 3 methyl acetate, 4 ethyl acetate, 5 butan-2-one, 6 ethanol, 7 pentanal, 8 ethyl butanoate, 9 butan-2-ol, 10 propan-1-ol, 11 hexanal, 12 2-methylpropan-1-ol, 13 butan-1-ol, 14 heptan-2-one, 15 heptanal, 16 3-methylbutan-1 ol, 17 (Z)-2-hexenal, 18 ethyl hexanoate, 19 pentan-1-ol, 20 octanal, 21 3-hydroxybutan-2 one, 22 heptan-2-ol, 23 ethyl heptanoate, 24 hexan-1-ol, 25 nonanal, 26 1-octen-3-ol, 27 acetic acid, 28 nonan-2-ol, 29 benzaldehyde, 30 octan-1-ol, 31

ethyl decanoate, 32

3-methylbutanoic acid



hexenal, (Z)-3-hexenal, (Z)-2-octenal; 8 ketones: propan-2 one, butan-2-one, heptan-2-one, nonan-2-one, decan-2-one, undecan-2-one, 3-hydroxybutan-2-one, tridecan-2-one; 11 esters: methyl acetate, methyl butanoate, ethyl acetate, propyl acetate, butyl acetate, ethyl propanoate, ethyl butanoate, ethyl pentanoate, ethyl hexanoate, ethyl heptanoate, ethyl decanoate; 2 acids: acetic and 3-methylbutanoic. Example of chromatograms of compounds identified in selected gooseberry varieties (red 'Karat' and yellow 'Darek' as sensorially the most acceptable, harvested in 2014) is given in Fig. 1.

Alcohols ethanol  $(9.0-228.6 \text{ mg kg}^{-1})$ , butan-2-ol  $(1.2-4.7 \text{ mg kg}^{-1})$ , ), 2-methylpropan-1-ol  $(0.01-3.1 \text{ mg kg}^{-1}),$  3-methylbutan-1-ol  $(0.5-7.0 \text{ mg kg}^{-1})$ , octan-1-ol  $(0.01-7.1 \text{ mg kg}^{-1})$ , acetic  $(0.01-33.4 \text{ mg kg}^{-1})$ ) and 3-methylbutanoic

 $(3.1-95.4 \text{ mg kg}^{-1})$  acids, in other chemical groups aldehydes ethanal  $(1.1-6.4 \text{ mg kg}^{-1})$ ,  $(E)$ -2-hexenal  $(0.5-3.1 \text{ mg kg}^{-1})$ , ),  $(Z)$ -2-octenal  $(1.3-1.9 \text{ mg kg}^{-1})$ , ketones butan-2-one  $(0.3-2.3 \text{ mg kg}^{-1})$ , esters ethyl acetate  $(0.04-7.9 \text{ mg kg}^{-1})$  and methyl acetate  $(0.05-$ 14.4 mg kg-<sup>1</sup> ) were present in high concentrations  $>2$  mg kg<sup>-1</sup>. The content of other compounds identified did not exceed 1 mg  $kg^{-1}$ .

## Comparison of volatiles in red, yellow and green fruiting varieties

To investigate the variability of volatile compounds in samples, two picking years for each cultivar were compared; then, the single cultivars were mutually compared, separately in 2014 and 2015. Similar to Hempfling et al. <span id="page-4-0"></span>Fig. 2 Distribution of chemical groups of volatile compounds in gooseberry cultivars harvested in 2014. For sample labelling, see chapter Gooseberry samples



[\(2013](#page-12-0)) and Nikfardjam et al. ([2013\)](#page-13-0), significant differences  $(p<0.05)$  were found between samples in the total content of compounds identified, as well as in the single chemical groups of compounds. The total content of compounds ranged from 21.9 mg kg<sup>-1</sup> ('Remarka') to 263.4 mg kg<sup>-1</sup> ('Alan') in red-fruiting, from 17.4 mg  $kg^{-1}$  ('Zlaty fik') to 139.2 mg  $kg^{-1}$  ('Invicta') in yellow-fruiting, and from 37.9 mg kg<sup>-1</sup> ('Mucurines') to 202.9 mg kg<sup>-1</sup> ('Rixanta') in green-fruiting varieties.

In contrast to Hempfling et al. [\(2013](#page-12-0)) and Nikfardjam et al. ([2013\)](#page-13-0), who found aldehydes and esters as dominating, alcohols and acids were quantitatively the most important in this study. Alcohols created 22–90% (w/w), 52–88% (w/w) and 49–93% (w/w), acids 1–62% (w/w),  $1-28\%$  (w/w) and  $2-46\%$  (w/w) in red/yellow/green fruiting varieties, respectively. Esters (1–36% w/w), aldehydes (1–18% w/w) and ketones (1–5% w/w) were mostly present at low quantity.

For illustrative purposes, the comparison of total content of single chemical groups of compounds identified in varieties from 2014 is shown in Fig. 2. As can be seen, content of alcohols predominate in most cultivars, and the content of ketones is very low in all varieties. The content of other groups is very variable. Generally, red-fruiting varieties had higher content of acids and esters, whilst yellow and green ones of aldehydes. Overall the composition of varieties was similar in both years, as confirmed by PCA analysis (see Fig. 3).

If we mutually compare single varieties within redfruiting, 'Alan' contained significantly  $(p<0.05)$  the highest total content of compounds owing to the especially high content of alcohols, namely ethanol, butan-2-ol and octan-1-ol. Conversely, 'Remarka' and 'Tamara' had the



Fig. 3 PCA score plot of 17 gooseberry varieties harvested in 2014–2015; for sample labelling, see chapter Gooseberry samples

lowest, mainly because of low content of acids. In the case of yellow fruiting, 'Invicta' had the highest total content, caused by the high content of alcohols (ethanol, butan-2-ol, 2-methylpropan-1-ol and 3-methylbutan-1-ol) and acids (3 methylbutanoic); on the other hand, 'Rodnik' and 'Zlaty fik' had the lowest, which was caused by low content of alcohols and nearly absence of acids. Interestingly, 'Rodnik' contained quite high content of esters, comparable to red varieties. In the case of green fruiting, 'Rixanta' had the highest total content owing to the especially high content of acids (3-methylbutanoic); conversely, 'Mucurines' has

very low quantity of alcohols causing the lowest total content of compounds. The observed differences probably followed from many factors. According to the Girard and Sinha [\(2006\)](#page-12-0), the content of fruit constituents could be influenced not only by cultivar, but also by environmental conditions as, e.g., climate, habitat, diseases and pest exposure. Provided that the storage and processing of samples were identical, in our case the differences between years of production (2014 vs. 2015) could be probably caused by the different climatic conditions in these years (see chapter Gooseberry samples).

To determine the statistically significant markers for characterization and differentiation of samples (red vs. yellow vs. green cultivars, and 2014 vs. 2015), PCA was performed using average concentrations of all volatile compounds identified in all 17 gooseberry varieties, representing the data matrix  $34 \times 52$  (for 34 samples and 52 variables-compounds). The cumulative contribution of variance of the first four PCs was 54.3%. The first two components explain 34.8% of total variability, where PC1 (22.8%) rather explains the variance between cultivars (red/yellow/green varieties), whereas the PC2 (12.0%) explains the variability within cultivars during 2 years.

Although significant differences ( $p < 0.05$ ) in contents of volatile compounds were found between cultivars, the differentiation of samples is ambiguous and unsatisfactory. As follows from score plot (Fig. [3\)](#page-4-0), there is apparent cluster of samples laying very close together in the left part of the plot, correlating negatively with PC1. This cluster includes most of yellow- and green-fruiting varieties, which thus were judged to be similar in contents of compounds identified. Only yellow-fruiting 'Invicta' is placed separately (both years) in right lower part, closer to red varieties and being especially rich in ethanol (104.4 and 74.6 mg  $kg^{-1}$ ), ), 2-methylpropan-1-ol (2.9 and 1.6 mg  $kg^{-1}$ ), 3-methylbutan-1-ol (6.9 and 7.0 mg  $kg^{-1}$ ) and 3-methylbutanoic acid (16.5 and 37.3 mg  $kg^{-1}$ ). Values in parenthesis are mean content in 2014 and 2015, respectively. With regard to the red-fruiting varieties, four of them ('Alan', 'Hinnonmaki Rot', 'Karmen' and 'Rolonda') are well separated; they lay in the right part of the graph correlating positively with PC1 and creating the second cluster. The others ('Karat', 'Krasnoslawjanskij', 'Remarka' and 'Tamara') were rather different and more similar to yellow/green varieties, being placed close, even mixed with them. It is probably caused by very low amount  $(< 0.08$  mg kg<sup>-1</sup>) of benzylalcohol, (E)-2-hexenal, propanal and acetic acid; in contrast to other red varieties, octan-1-ol, propan-1-ol and 3-methylbutan-1-ol were not detected in these varieties. We can consider that there could be possible to distinguish red from yellow/green varieties based on composition of compounds identified. Green- and yellow-fruiting varieties are not easy distinguishable in such way. Most of the varieties placed in right part of the plot showed detectable off-flavour, as mentioned later. On the other hand, the small (less significant) differences between picking years (2014 vs. 2015) are visible in the plot (Fig. [3](#page-4-0)); both years lay close to each other in most cultivars. This fact is especially clear in yellow/green varieties; in the case of red ones significant differences  $(p<0.05)$  were found.

If we consider three significant PCs, the PC1 was highly correlated with benzylalcohol (0.89), propyl acetate (0.89), benzaldehyde (0.79), hexan-1-ol (0.72), propanal (0.66), 3-hydroxybutan-2-one (0.62), ethyl acetate (0.61); the PC2 was correlated with ethyl acetate (0.68), 3-hydroxybutan-2 one  $(0.65)$ , 3-methylbutan-1-ol  $(-0.70)$ , pentan-1-ol  $(-0,70)$ ; PC3 with acetic acid  $(0.74)$ , propan-1-ol  $(0.73)$ and methyl acetate (0.69). The content of these 12 compounds is probably the most variable in samples and they could be considered to be the most important for differentiation between samples. The comparison of these selected volatiles (using ANOVA) in all varieties is given in Table [1](#page-6-0).

Alcohols hexan-1-ol and pentan-1-ol were identified nearly in all varieties, mostly in quite low quantities  $(<50 \ \mu g \ kg^{-1})$ . Benzylalcohol and propan-1-ol were detected only in red varieties, with the exception of yellow 'Invicta', where about 400  $\mu$ g kg<sup>-1</sup> of benzylalcohol was found in both years. The content of benzylalcohol ranged from 32.3  $\mu$ g kg<sup>-1</sup> in 'Karat' to 694.4  $\mu$ g kg<sup>-1</sup> in 'Rolonda'. Propan-1-ol was found in 'Alan', 'Remarka' and 'Tamara' at low concentrations about  $5-8 \mu g kg^{-1}$  and 'Karmen' at  $>100 \mu g kg^{-1}$ . 3-methylbutan-1-ol was identified only in five varieties: 'Rolonda' and 'Invicta' (about  $2-7 \mu g kg^{-1}$ ), 'Hinnonmaki Rot', 'Citronovy obři' and 'Mucurines' ( $>480 \mu g kg^{-1}$ ). With regard to the aldehydes, benzaldehyde was identified in most varieties in range 3–60  $\mu$ g kg<sup>-1</sup>; propanal was present only in several varieties; its content was very variable (about  $2-700 \mu g kg^{-1}$ ). Also, 3-hydroxybutan-2-one was present in most varieties (about 2–60  $\mu$ g kg<sup>-1</sup>), which was significantly higher in red 'Alan' ( $>$ 100 µg kg<sup>-1</sup>). Esters methyl and ethyl acetate were present in all varieties, and their amounts were variable  $(2-1700 \text{ µg kg}^{-1})$ ; conversely, propyl acetate was present only in several varieties at very low quantity  $(2-15 \text{ µg kg}^{-1})$ . Acetic acid was detected only in several varieties; significantly highest amount was in red 'Rolonda and 'Karmen'  $(7-33 \text{ mg kg}^{-1})$ , the others about 10–20  $\mu$ g kg<sup>-1</sup>.

Another PCA was performed with these 12 compounds (data matrix  $34 \times 12$ ), which resulted in three significant PCs accounting for 45.2, 21.0 and 17.2% of variance, respectively, which express satisfactory 83.4% of total variability. PCA score plot for the first two components

## <span id="page-6-0"></span>Table 1 Comparison of selected volatile compounds identified in gooseberry varieties



## 1902 Chem. Pap. (2017) 71:1895–1908



#### Table 1 continued

Values identified by an asterisk (\*) mean content in mg kg<sup>-1</sup>; the results are expressed as the mean  $\pm$  standard deviation (*n* = 9); different capital letters in the same column indicate significant differences  $(p < 0.05)$  between the picking years (2014–2015) within the same cultivar; different small letters in superscript/subscript in the same column indicate significant differences ( $p < 0.05$ ) between the cultivars in 2014/2015, respectively

nd not detected

(not presented) is very similar to previous one (see Fig. [3](#page-4-0)); two apparent clusters are distinguished here. First one, correlating negatively with PC1, includes yellow/green varieties, indicating their great similarity in composition of compounds identified. The second cluster is placed in the right part of the graph correlating positively with PC1. It includes most of the red varieties. The special position of yellow fruiting 'Invicta' was confirmed here, as it has the highest total content of all compounds identified.

## Comparison of sensory characteristics in red, yellow and green fruiting varieties

Another partial aim of this study was to evaluate sensory quality of samples using descriptive sensory methods. The list of evaluated attributes comprised appearance and colour, texture supplemented with two mouthfeel attributes (firmness and crispiness), taste and odour with three flavour characteristics (sweet, acid/sour, astringent), possible offflavour and overall acceptability. The results are summarized in Table [2](#page-9-0). As in the case of volatile compounds in samples, two picking years for each cultivar were compared; then, the single cultivars were mutually compared, separately in 2014 and 2015. The similarities/differences of red vs. yellow vs. green varieties were also judged.

Appearance and colour are significant sensory properties creating the first impression of fruits. As mentioned before, the size, shape and colour of gooseberries depend mainly on variety (Girard and Sinha [2006\)](#page-12-0); the larger fruits are preferred (Harb and Streif [2004](#page-12-0)). Appearance was evaluated taking into consideration mainly size and shape; large fruits of regular oval shape, with bright surface without injury and smooth skin with/without fine hairs, were considered as excellent. The colour of pulp is often identical with the skin, it becomes more intense during ripening and fruits reach their typical colour in full ripeness. Colour of samples was difficult to compare owing to three types of varieties evaluated; moreover, colour intensity was not uniform even in the same sample, as it is influenced by the location of the fruit in a shrub (Girard and Sinha [2006](#page-12-0)). For these reasons, colour was evaluated separately, from the hedonic point of view, using scale from atypical to typical for a given variety. Characteristic, intense, homogeneous colour was considered as excellent. While in the case of yellow and green varieties, pale colour is well evaluated; in red ones, the darker is better (Harb and Streif [2004\)](#page-12-0).

In the case of red varieties, 'Karat' was evaluated as having the best appearance (94.4; 66.8%) as well as the colour (90.2; 71.4%). Values in parenthesis are mean evaluations in 2014 and 2015, respectively. This variety should have large, less usual pear shaped fruits; its colour varies from pink to red to purple (Hanč et al. [2013](#page-12-0)). In our case, the fruits were large with deep red colour, which was probably the reason of excellent evaluation. Conversely, red 'Karmen' was evaluated as having the worst (less good) appearance (28.5; 47.5%) and colour (39.1; 61.1%). This variety should have medium size and oval shape (Hanč et al.  $2013$ ). In our case, the fruits were large and oval; however, pale red colour was probably the reason of bad evaluation. In the case of yellow varieties, 'Darek' (77.7; 69.2%) and 'Rodnik' (77.7; 71.4%) were evaluated as the best in appearance as well as in colour ('Darek' 71.5; 64.3%, 'Rodnik' 73.2; 70.2%). Both these varieties have

large fruits; 'Darek' is round shaped, yellow-green and 'Rodnik' of oval shape and deep yellow in full ripeness (Hanč et al. [2013](#page-12-0)). Conversely, 'Zebin' had the worst appearance (35.3; 28.5%), although it had very large fruits. Intense hairy skin was probably the cause of bad evaluation. The colour was yellow-green, evaluated as less good (38.9; 27.2%). The colour and appearance of 'Zebin' were the worst of all varieties. Appearance and colour of all three green varieties were evaluated similarly as good/very good (in range 50.4–83.3%), although only 'Mucurines' should have bright green colour. The other two varieties are ranked to specific group of yellow-green varieties according to their rather yellow-green colour (Girard and Sinha [2006;](#page-12-0) Hanč et al. [2013](#page-12-0)). However, in our case all three varieties were of medium size, yellow-green colour, with smooth skin practically without hairs. The difference in colour between green 'Mucurines' and other two ones was hardly perceptible and insignificant.

The texture of gooseberries depends mainly on variety. The pulp is soft in full ripeness; however, the texture is also related to skin firmness, which influences the overall firmness and crispiness of fruit. The skin becomes softer during ripening, which determines the use; fruits with softer skin are suitable for direct consumption; those with firmer skin are preferred for processing (Girard and Sinha [2006](#page-12-0)). The softening during storage was also observed by Harb and Streif ([2004\)](#page-12-0), which put emphasis on quickness of processing.

The texture was evaluated owing to the suitability for direct consumption, putting stress on soft pulp and firm skin, which keeps desirable crispiness. In red varieties texture of 'Karat' (86.1; 59.2%), 'Rolonda' (75.0; 71.4%) and 'Tamara' (72.2; 69.7%) were evaluated as very good, which was in accordance with the good evaluation of firmness and crispiness. In yellow varieties, 'Darek' (77.7; 71.4%) and 'Rodnik' (72.2; 71.4%) were best evaluated with firm and crispy fruits. Conversely, red 'Karmen' (28.5; 52.2%) and yellow 'Invicta' (57.1; 43.1%) and 'Zebin' (51.9; 42.8%) were evaluated as the worst; the fruits were too soft with no crispiness. In green varieties, 'Prima' had the best texture (66.6; 61.5%) with good firmness and crispiness; conversely, 'Rixanta' was evaluated very badly (38.8; 28.5%), the worst of all varieties. Also, its fruits were too soft. As can be seen, very soft texture is negatively perceived by assessors; too soft fruits were evaluated as unsatisfactory. That is in accordance with Harb and Streif [\(2004](#page-12-0)), who identified the fruit firmness as one of the main indicators of gooseberry quality.

The main attention was paid to taste and aroma (flavour) owing to the intended comparison with the volatile compounds identified. If we consider fully ripe fruits, provided that all samples were harvested and stored in the same way, these characteristics depend mainly on variety (Girard and



<span id="page-9-0"></span>

(b)



#### Table 2 continued

 $(h)$ 





The results are expressed as mean  $\pm$  standard deviation ( $n = 22$ ). Different small letters in superscript/subscript in the same column indicate significant differences ( $p < 0.05$ ) between the cultivars in 2014/2015, respectively

nd not detected

Sinha [2006](#page-12-0)); the taste of gooseberries is characteristic mildly astringent because of tannins, sweet and/or acidic depending on the variety (Harb and Streif [2004\)](#page-12-0). Characteristic, pleasant gooseberry taste/aroma without any offflavour was considered as excellent. Because the taste of gooseberries could be either sweeter or more acidic (Harb and Streif [2004\)](#page-12-0), the intensity of these descriptors were evaluated separately, similarly to astringency, which is characteristic for gooseberries, but in strong intensity could be unpleasant.

Red 'Karat' (68.8; 57.1%) had the best taste in both years. This variety should have sweet–sour taste (Hanč et al. [2013](#page-12-0)); in our case it was rather sweet (73.2; 72.4%) and the acidity was low (33.6; 42.8%). 'Tamara'

(31.5; 30.9%) had the worst taste with low sweetness (29.8; 27.5%) and higher astringency (43.8; 47.5%). No mention was found in the literature about typical taste of this variety. The odour of 'Remarka' (59.2; 64.8%) was best evaluated in both years; its odour used to be described as very aromatic (Hanč et al. [2013\)](#page-12-0); conversely, 'Rolonda' had the worst odour (28.5; 47.1%) probably because of off-flavour. Between yellow varieties, 'Darek' had the best taste (55.5; 61.5%) as well as the odour (58.7; 67.4%) in both years. This variety should have sweet–sour taste (Hanč et al. [2013](#page-12-0)); in our case, it was rather sweet (58.5; 64.0%) with low acidity  $(33.2\%; 31.8\%)$ . 'Citronovy obři' had the worst taste (37.1; 33.5%). This variety should also have sweet–sour taste (Hanč et al.  $2013$ ); however, in our case it was very acid (72.4; 66.8%) and astringent (69.3; 64.7%). Although 'Invicta' was quite sweet (79.4; 71.4%), its taste (42.8; 47.1%) and odour (28.5; 41.6%) were not well evaluated probably because of off-flavour. The taste of this variety is often described as sweet, but bland (Hanc̆ et al.  $2013$ ). In the case of green varieties, 'Mucurines' could be labelled as having the best taste (50.6; 46.7%) and odour (62.4; 57.1%). According to the Nikfardjam et al. ([2013](#page-13-0)), this variety showed strong grassy aroma, in accordance with (Hanč et al. [2013\)](#page-12-0); its taste was mildly sweet  $(59.2; 42.8%)$  and sour  $(27.6;$ 57.1%). The evaluation of other two green varieties was worse; 'Prima' was found to be very acid (75.9; 68.4%) and astringent (65.5; 60.1%), while 'Rixanta' had offflavour, although it was very sweet (79.8; 71.4%). As mentioned before, these two varieties do not have typical green colour, which could also influence evaluation of taste and aroma (Girard and Sinha [2006](#page-12-0); Hanč et al. [2013](#page-12-0)).

The mild but obvious off-flavour was detected in red 'Alan' (14.2; 28.5%), 'Hinnonmaki Rot' (31.4; 28.5%), 'Krasnoslawjanskij' (21.3; 44.8%) and 'Rolonda' (18.1; 14.2%), yellow 'Invicta' (14.2; 16.9%) and green 'Rixanta' (17.2; 14.2%) varieties in both years, described as fermented, slightly bitter and/or acid. Although the samples were cold stored for a very short time, this fact is probably related to initiating fermentation process (Harb and Streif [2004\)](#page-12-0) and seems to be connected with the high ethanol content. Nikfardjam et al. ([2013](#page-13-0)) relate the possible overripe off-flavour to the ratio between (Z)-3-hexenal and ethyl acetate, while the pentan-2-one and heptan-2-one content are connected with the musty off-flavour; these defects were not detected in this study. As expected, the presence of off-flavour, although mild, negatively influenced the evaluation of taste and aroma. That is in accordance with Harb and Streif ([2004\)](#page-12-0), who identified the possible off-flavour as one of the main indicators of gooseberry quality.

Finally, the overall acceptability was evaluated taking into consideration all evaluated properties. Red 'Karat' (76.2; 77.1%) and yellow 'Darek' (74.4; 71.6%) could be labelled as the best of all varieties. They were well evaluated in both years with very good all of evaluated sensory properties. On the other hand, red 'Karmen' was concluded to be the least acceptable (28.5; 32.4%) as evaluated very badly in all characteristics. Contrary to Hempfling et al. ([2013\)](#page-12-0) who considered red fruiting varieties as the most interesting for commercial purposes, because they were the most preferred by consumers, no obvious preference was found between red, yellow and green types in this study.

The results of sensory evaluations were tested by PCA to investigate which sensory descriptors correlate to each other and which of them contribute to overall sensory quality and acceptability of samples. PCA was performed using average ratings of all sensory characteristics in all 17 gooseberry varieties in both years (data matrix  $34 \times 12$ ). Three PCs were derived accounting for 34.0, 25.8 and 14.4% of the variance, respectively, which cumulatively explained satisfactory 74.2% of the total variability. The PC1 was highly correlated with appearance  $(-0.87)$ , colour  $(-0.80)$ , taste  $(-0.66)$ , texture  $(-0.68)$ , firmness  $(-0.60)$  and overall acceptability  $(-0.84)$ . The PC2 was associated with sweet  $(0.87)$  and astringent  $(-0.84)$  tastes and crispiness  $(-0.65)$ . As expected texture, firmness and crispiness highly correlate to each other, as well as the colour vs. appearance and taste vs. odour. Sweetness correlates negatively with acid and astringent tastes; sweeter and more astringent/ acid samples are well divided along the PC2. The overall acceptability strongly correlates with PC1; the appearance, colour, taste and odour contribute the most to the overall acceptability. Harb and Streif ([2004](#page-12-0)) identified the fruit firmness, sweet-acid taste balance and the possible off-flavour as the main indicators of sensory quality of gooseberries. In this study, PCA did not confirm the significance of texture and off-flavour in acceptability of gooseberries. However, it confirmed the importance of sweet/acid taste, as assessors preferred sweeter, less acidic gooseberries. Off-flavour was detected only in a few samples in low intensity and probably does not influence significantly acceptability of samples.

Although ANOVA indicates significant differences between varieties, there is no clear differentiation of samples according to the red/yellow/green varieties. PC1 correlates with the overall acceptability, PCA such confirmed red 'Karat' and yellow 'Darek' as the most acceptable varieties. The differences between years of production (2014 vs. 2015) were mostly small or not significant, as confirmed by ANOVA analysis.

# <span id="page-12-0"></span>The contributions of compounds identified to the sensory quality of samples

To better estimate which compounds could contribute to flavour/acceptability of samples, the PCA was performed using the instrumental and sensory data of 17 gooseberry varieties in both years (data matrix  $34 \times 64$ ), and odour activity values (OAVs) were calculated by dividing contents of given compound in the sample by its odour threshold acquired from the literature (Jensen et al. 2000; Belitz et al. 2009; Sanchez-Palomo et al. [2010;](#page-13-0) Hempfling et al. [2013;](#page-13-0) Nikfardjam et al. 2013; Sádecká et al. [2014](#page-13-0)). Nikfardjam et al. ([2013\)](#page-13-0) identified in gooseberries 17 compounds as aroma active; similarly, Hempfling et al.  $(2013)$  identified 10 compounds with OAVs  $>1$ . Hempfling et al. (2013) characterize the typical gooseberry aroma as combination of green and fruity notes, where fruity aroma becomes stronger during ripening. (Z)-3-hexenal and short chain ethyl and/or methyl esters, especially methyl and ethyl butanoate, are considered as the carriers of this aroma. Nikfardjam et al. [\(2013](#page-13-0)) also identified (Z)-3-hexenal and ethyl acetate as responsible for the aroma of gooseberries. In accordance with these studies (Z)-3-hexen-1-ol (OAVs 1-3; geranium), 1-octen-3-ol (OAVs 6-14; mushroom-like), (Z)-3-hexenal (OAVs 794-5168; grassy), hexanal (OAVs 1-2; grassy, citrus-like), heptan-2-one (OAVs 1-2; fruity, sharp, herbaceous), methyl butanoate (OAVs 1-11; fruity, green), ethyl butanoate (OAVs 6-199; fruity, pineapple-like), methyl acetate (OAVs 1-8; fragrant, fruity) and ethyl acetate (OAVs 13-1589; fruity, pear like) were recognized as aroma active in this study. Their aroma description is in parenthesis. Moreover, another 7 compounds were proposed as possible contributors to gooseberry aroma as their OAVs were  $>1$ : ethanol (OAVs 1-2; alcoholic), octan-1-ol (OAVs 20-65; citrus, spicy, herbaceous), 3-methylbutan-1-ol (OAVs 1-2; burnt, alcohol), ethanal (OAVs 162-912; fruity, pungent), propanal (OAVs 1-5; fruity, pungent), acetic acid (OAVs 150-477; fruitysour, vinegar) and 3-methylbutanoic acid (OAVs 95-2738; sweet, acid, rancid).

According to the PCA, between these compounds (Z)-3 hexen-1-ol, (Z)-3-hexenal, heptan-2-one, methyl butanoate, ethyl butanoate, methyl acetate, ethyl acetate, ethanol and ethanal correlate positively with flavour/acceptability of samples. As in Nikfardjam et al. [\(2013](#page-13-0)), (Z)-3-hexenal and ethyl acetate had the highest OAVs with the grassy and fruity aroma, respectively, while 1-octen-3-ol, hexanal, octan-1-ol, 3-methylbutan-1-ol, propanal, acetic and 3-methylbutanoic acid could negatively influence the flavour, as they correlate negatively with flavour/acceptability of samples. 3-methylbutanoic acid with its rancid aroma had the highest OAV.

#### **Conclusions**

Only a few studies on the volatile/aroma compounds of gooseberry have been published so far, as well as on their connection with the flavour of these fruits. This work is a complex study focused on selected varieties intended to be grown in the Czech Republic. The combination of the instrumental assessment of volatile compounds and sensory evaluation with the great emphasis on flavour was used for characterization of samples. In total, 52 volatile compounds were identified and quantified, with quantitatively predominating alcohols and acids. Based on PCA and calculation of OAVs, 9 of them were supposed to contribute to flavour of samples as having the  $OAVs > 1$  and correlating positively with sensory evaluation of flavour.

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