Sensory and instrumental analysis of eight genotypes of red raspberry (*Rubus idaeus* L.) fruits

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Abstract

BACKGROUND: There is a search for raspberry cultivars with high sensory quality. The best way to determine sensory quality is by descriptive analysis. To perform sensory analysis by a trained panel is, however, not always feasible. Therefore, there is a need for instrumental measurements that correlate with sensory attributes.

OBJECTIVE: To characterize eight genotypes of raspberry (*Rubus idaeus* L.) and to correlate sensory attributes with instrumentally determined quality.

METHODS: Raspberry fruits were analysed by descriptive sensory analysis and by instrumental measurements, i.e. colour, total monomeric anthocyanins, soluble solids (SS), pH, titratable acidity (TA) and volatile compounds. The relationships between sensory attributes and instrumentally determined quality were determined by partial least square regression and by univariate correlation analysis.

RESULTS: Sour and green odours/flavours versus chemical and cloying odours/flavours described most of the sensory variation of the raspberry genotypes. TA correlated with acidic taste, astringency and flavour intensity. SS/TA was positively correlated with sour flavour and sweet taste and negatively correlated with acidic taste and astringency. C6-aldehydes and (*Z*)-3-hexen-1-ol correlated positively with green flavour. β-ionone and α-ionone correlated with flower odour and flavour, respectively.

CONCLUSIONS: Eight raspberry genotypes were characterized. Important sensory attributes could be predicted by instrumental measurements.

Keywords: raspberry; sensory profiling; volatile compounds; instrumental analysis; correlation

1. Introduction

The interest and production of raspberries (*Rubus idaeus* L.) are steadily increasing and the production worldwide is now more than 0.8 million tons, an increase from 0.5 million tons in 2010 (http://www.fao.org/faostat/). At the same time, there is a search for new raspberry cultivars which both have good cultivation properties and are attractive for the consumers. High sensory quality is an important asset for the consumer. Sensory properties of raspberries comprise appearance, odour, flavour and texture, which together determine the attractiveness of the berries [1]. The sensory characteristics are determined by the chemical composition of the berries. Anthocyanins, mainly cyanidin glycosides, are responsible for the red-purple colour of raspberries [2, 3]. Flavour is defined by taste and odour-active compounds, i.e. volatile compounds detected by the olfactory system. Sugars and acids are the main taste compounds in raspberries, but phenolic compounds may contribute to bitter taste and astringency [4-6]. Fructose, glucose and sucrose give raspberries their sweet taste [4, 5, 7]. The perception of sweetness will, however, be modified by organic acids, mainly citric acid, and odour-active compounds [5, 7, 8]. Nearly 300 volatile compounds have been identified in raspberry fruits, with major classes of compounds being terpenes, C13 norisoprenoids, acids, alcohols and esters [8]. The raspberry aroma is due to a mixture of odour-active volatile compounds, i.e. with sufficient low odour threshold values to be detected by humans. There have been several attempts to identify the most important flavour compounds in raspberries and 4-(4-hydroxyphenyl)-2-butanone (raspberry ketone) and α- and β-ionone are stated to be primary character impact compounds of raspberries [9, 10]. Other compounds contributing to raspberry aroma are benzyl alcohol, (*Z*)-3-hexen-ol, acetic acid, linalool, geraniol, α- and β-pinene, α- and β-phellandrene and β-caryophyllene. However, to determine the most important flavour compounds is challenging because aroma is due to a mixture of compounds and aroma active compounds can be present in very low concentrations. Furthermore, various analytical techniques have been used to extract and detect volatile compounds in raspberries and direct comparison between different studies may not be straightforward [4, 7, 10-15].

The most complete and objective way to determine sensory quality is descriptive analysis conducted by a trained sensory panel. To perform sensory analysis by a trained panel is, however, not always feasible. Therefore, there is an aim to identify chemical compounds and instrumental measurements that correlate with sensory attributes and thereby can be used to predict sensory quality. As an example, colour can be determined by the CIE L*a*b* colour system by instrumental analysis. Sweet taste is assumed to correlate with sugar content, which easily can be determined as soluble solids (SS) with a refractometer (°Brix) and acidity is influenced by contents of organic acids and can be determined as titratable acidity (TA). Volatile compounds measured by GC-MS are supposed to correlate with odour and flavour of the samples. These simpler, instrumental methods can be used to determine sensory quality on many samples, for example in breeding to evaluate new crossings and cultivars, in studies of cultivation practices, in storage experiments etc. However, for these measurements to be meaningful, they must coincide with human perception, i.e. sensory properties. There are a few reports on both chemical and sensory evaluation of raspberries [4, 5, 16], however, in these studies the sensory analysis is quite simple (only a few attributes, ranking) and/or performed on a small number of cultivars.

The aims of the present study were 1) to characterize fruits of eight genotypes of red raspberry (*Rubus idaeus* L.) and 2) to correlate sensory attributes of raspberries with instrumentally determined quality (soluble solids, titratable acidity, pH, volatile compounds, total content of anthocyanins and colour).

2. Materials and methods

2.1 Chemicals and reagents

(*E*)-2-Hexenal, (*Z*)-3-hexen-1-ol, (*Z*)-3-hexenal, (*Z*)-3-hexenyl acetate, (*E*,*E*)-2,4-hexadienal, 3-methyl-2-butenyl acetate, 3-methylbutanal, acetic acid, trans α-ionone, α-phellandrene, α-pinene, trans β-ionone, β-pinene, β-caryophyllene, ethyl acetate, ethyl heptanoate, hexanal, D-limonene, methyl acetate, β-myrcene and p-cymene were purchased from the Sigma-Aldrich company. Sodium phosphates, potassium chloride and sodium acetate were obtained from Merck KGAa (Darmstadt, Germany). All chemicals and solvents were of analytical or HPLC grade and water was of Milli-Q quality (Millipore Corp., Cork, Ireland).

2.2 Berries

Red raspberries (*Rubus idaeus* L.) were grown at the experimental field at NIBIO Apelsvoll, Norway (59º40'N, 10º40', 250 m above sea level). The field was established in spring 2015. The plants were planted on low, raised beds mulched with woven black polyethylene at a planting distance of 400 x 50 cm. Each experimental plot was randomly distributed and consisted of 2.5 m running row with 6 plants, and with three replications of each plot per genotype. The shoot density was regulated in spring to 4 primocane shoots per plant (i.e. 8 shoots per m row). The plants were watered and fertilized via an automatic drip irrigation system. The electric conductivity (EC) of the fertilizer solution was maintained at 1.5 mS cm^{-1}, and it was applied 1-3 times weekly (according to irrigation needs) from mid-May. Experimental harvesting of all plots was done three times a week during the season.

The genotypes were new cultivars and selections from Norway and UK, and the older, well established cultivars Glen Ample, Tulameen and Veten (Table 1). All cvs. are suited for fresh consumption, except for 'Veten' that was included as a typical cultivar for industrial purposes. Date of 50% harvested fruits was August 6th for 'Glen Carron' and 'Veten', August 8th for 'Glen Ample' and 'Glen Fyne', August 12th for 'Anitra', August 17th for 'Tulameen', August 21th for 'Ninni' and August 24th for RU044 03090. On August 14th, 12 punnets (300 g berries) of each genotype were picked. The berries were cooled to 4 °C, before transportation to Nofima and storage overnight at 4 °C. The next day sensory analysis and analysis of volatile compounds were performed (6 punnets) and colour of whole berries were measured (2 punnets). Berries for other analyses were frozen at -20 °C prior to analysis (4 punnets).

2.3 Sensory analysis

The eight raspberry genotypes were analysed by a trained sensory panel with ten professional assessors using a quantitative descriptive method, ISO 13299:2016E. The assessors have been selected and trained according to guidelines in ISO 8586:2012(E) and employed exclusively to work as sensory assessors. The assessors take part in sensory analyses 12 h per week and has between 3 and 25 years of experience using descriptive analysis on various kinds of food and beverages. The sensory laboratory has been designed according to guidelines in ISO 8589 (2007) with separate booths and has electronic data registration (EyeQuestion®, Logic8 BV, Wageningen, The Netherlands).

Prior to analysis, the assessors were trained in definition of the chosen sensory attributes by testing samples with supposed varying intensity of the sensory attributes ('Ninni' and 'Veten'), for agreeing on the definitions of each attribute and variation in attribute intensity. Description of the 22 sensory chosen attributes is given in Table 2.

The raspberries were removed from cold storage two hours before serving and were room-tempered (18 ± 2 °C) at serving. The berries were served on white plastic trays with lid labelled with a random three-digit number. The panellist received five berries of uniform size of each sample, randomly picked from the six punnets. At first, odour and colour were assessed on all berries. Taste and flavour were assessed on 2-3 berries, then finally texture was assessed on the remaining berries.

Each genotype was served in duplicate. The samples were served in randomised order (according to sample, assessor and duplicate) in four rounds with four samples in each round. The palate was rinsed with unsalted crackers and lukewarm water between samples. The assessors recorded their results at individual speed on a 15 cm non-structured continuous scale. The data registration system (EyeQuestion®) transformed the responses into numbers between 1 (low intensity) and 9 (high intensity).

2.4 Colour

Surface colour of both whole berries and homogenised berries were measured using a digital colour imaging system (DigiEye, VeriVide Ltd., Leicester, UK). Colour of whole berries was determined on berries in the punnet and was the average of the colour of all berries in the punnet. The samples were placed in a light-box with standardised daylight (CIE D65) with diffuse lighting and photographed with a calibrated digital camera (Nikon D7000, 35 mm lens, Nikon Corp., Japan). Colour measurements in the CIE colour space ($L^*a^*b^*$ values) were made on the pictures using DigiPix software (version 2.63).

L^* describes lightness, where lower values indicate darker colour (0 = black) and higher values indicate lighter colour (100 = white). Hue angle (arctan (b^*/a^*)) designates colour shade where low values (Hue

= 0°) indicate a red-bluish colour and high values (Hue = 90°) indicate a yellow colour. Chroma ($(a^{*2} + b^{*2})^{1/2}$) shows transition from grey (low values) to pure colour (high values).

2.5 Soluble solids, pH and titratable acidity

Berries thawed overnight at 4 °C were homogenized in a food processor and centrifugated at 39200*g* for 10 min (Avanti J-26 XP). The supernatant was used for analyses of soluble solids (SS), pH and titratable acidity (TA). pH was determined at room temperature with a pH meter (827 pH lab., Metrohm, Switzerland). Content of SS was determined using a digital refractometer (RE40, Mettler Toledo Inc., Japan) and expressed as °Brix (%). TA was measured by titrating diluted supernatant (3 mL in 30 mL distilled water) with 0.1 M NaOH to pH 8.0 using an automatic titrator (Mettler Toledo T50, Switzerland). The concentration of TA was expressed as g citric acid equivalents per 100 g. The genotypes were homogenized and analysed in duplicate, i.e. berries from two punnets (each 300 g).

2.6 Total monomeric anthocyanins (TMA)

Berries, homogenised in a food processor (10 g), was added methanol (20 mL) and homogenised for 30 s with a Polytron homogenizer (PT3100, Kinematica AG, Littau Switzerland). After centrifugation (39200*g* for 10 min, Avanti J-26 XP, Beckman Coulter Inc., USA), the supernatant was collected and the pellet re-extracted with 70% methanol in water (v/v) (20 mL). The supernatants were combined and the volume of the extract was made up to 50 mL with 70% methanol (v/v).

TMA was determined by the pH-differential method [17]. The extracts were diluted in two buffers; 0.025 M potassium chloride (pH 1) and 0.4 M sodium acetate (pH 4.5). After 30 min at 20–22 °C, absorbance at 520 and 700 nm was measured (Agilent 8453 Spectrophotometer, Agilent Technologies). The genotypes were extracted and analysed in duplicate, i.e. berries from two punnets (each 300 g). The concentration of TMA was calculated as mg cyanidin-3-glucoside equivalents per 100 g of fresh weight (mg/100 g fw).

2.7 Analysis of volatile compounds

Analysis of volatile compounds was performed by a dynamic headspace technique. The raspberries (30 ± 1 g, 4-8 berries) were cut in two and weighed into an Erlenmeyer bottle (250 mL). Internal standard (ethyl heptanoate, 0.4 μg/μL) was added (2.0 μL). The samples were purged with nitrogen (100 mL/min) for 30 min at ambient temperature (20-22 °C) and volatile compounds were collected on an adsorbent tube (Tenax GR, 60-80 mesh, Alltech, Deerfield, IL, USA).

The volatile compounds were desorbed from the adsorbent tubes in an automatic thermal desorber (Markes TD100 Thermal Desorber, Markes Int. Ltd., UK) and transferred to an Agilent 6890 GC interfaced with an Agilent 5973 Mass Selective Detector (EI, 70eV) (Agilent Technologies, USA). Positive ions were recorded in the range m/z 30-400 at an acquisition rate of 3.1 scans/s. The volatile compounds were separated on a DB-WAXetr column (30 m, 0.25 mm i.d., 0.5 µm film, Agilent J&W GC columns) with the following temperature gradient: 30 °C for 10 min, 1 °C/min to 40 °C, 3 °C/min to 70°C, and 6.5 °C/min to 230 °C, hold time 5 min. Total ion chromatographic peaks were integrated by the Agilent Chemstation software. Compound identification was based on mass spectra match with the NIST98 Mass Spectral Library and comparison with authentic standards when available (see section 2.1).

The raspberry genotypes were analysed in triplicate. Semi-quantitative amounts of volatile compounds were calculated based on peak areas relative to internal standard (ethyl heptanoate, 0.8 µg), the weight of raspberries (ca. 30 g) and total volume of purging gas (3 L) giving the unit µg/(g x L).

2.8 Statistical analysis

Two-way analysis of variance (ANOVA) was performed to determine significant differences ($p < 0.05$) in sensory attributes between raspberry genotypes (EyeQuestion®, Logic8 BV). The model included genotype as a fixed effect and panellist and genotype x panellist as random effects. Significant differences between average response values were evaluated by Tukey's multiple comparisons test. To illustrate the variation among raspberry genotypes, significant sensory attributes were analysed by Principal component analysis (PCA). Partial Least Square (PLS) regression analysis was performed to explain the relations between instrumental measurements (X-variables) and sensory attributes (Y-variables). The X-variables were weighed by 1/standard deviation before analysis. Full cross-validation was used to validate the PLS model. PCA and PLS regression were performed using The Unscrambler software (The Unscrambler®X version 10.4.1, CAMO Software AS, Oslo, Norway). Univariate correlation analysis (linear regression) between sensory attributes and instrumental measurements was performed by Minitab® Statistical Software version (version 18.1, Minitab Ltd., Coventry, UK).

3. Results and discussion

3.1 *Sensory profile*

ANOVA of the sensory data revealed that there were significant differences between the raspberry genotypes in all attributes, except for flower odour and flavour intensity (Table 3).

Principal component analysis (PCA) showed that PC1 and PC2 described 77 and 11% of the variation among the samples, respectively (Fig. 1). Chemical and cloying odours and flavours versus firmness and sour and green flavours and odours described most of the variation in PC1, while sweet taste and sour and flower flavours versus acidic taste and astringency described the variation in PC2 (Fig. 1A). 'Veten' was characterised by chemical and cloying flavours and odours and high odour intensity. 'Glen Carron' also had high levels of these attributes. 'Veten' was the less firm and the most juicy of the samples tested (Table 3). 'Ninni' and 'Glen Fyne' were characterised by sour flavour, sweet taste, flower flavour and high firmness. 'Glen Ample' and 'Anitra' were described by sour odour and green flavour and odour. 'Tulameen' was the cultivar with the highest scores for acidic taste and astringency.

'Glen Ample', which is the dominating variety grown in Norway, and 'Glen Carron' had the highest colour intensity and whiteness and the lowest intensity of colour hue, i.e. was the most yellowish red and brightest of the berries tested. The berries of 'Veten' and 'Ninni' were the darkest and most bluish red with the lowest colour intensity.

A previous study of five raspberry cultivars showed that high ratings of overall impression were obtained when the fruits were sweet, firm, had good appearance, red colour and strong raspberry aroma and fruitiness and low astringency [4]. In a study where preference mapping was used to investigate the relationship between consumer preferences and sensory description, it was found that floral aroma, raspberry flavour, colour uniformity, shine and sweet taste were the sensory attributes contributing the most to acceptability of fresh raspberries [1]. Green aroma, on the other hand, was a negative driver of liking. Of the cultivars investigated in the present study, 'Ninni', 'Glen Fyne' and RU044 03090 would thus be expected to be preferred by the consumers, while 'Tulameen' and 'Glen Ample' might be perceived to be too astringent and acidic.

3.2 *Soluble solids, pH and titratable acidity*

pH in the raspberries varied from 2.79 in 'Tulameen' to 3.02 in 'Ninni' (Table 4). SS was from 8.2 g/100 g in 'Glen Ample' to 10.2 g/100 g in RU044 03090. TA was lowest in 'Ninni' (1.77 g/100 g) and highest in 'Tulameen' (2.80 g/100 g), which also had the highest (5.5) and lowest (3.5) SS/TA ratios, respectively. The levels of SS, TA and pH in the raspberries in the present study were similar to values previously found in berries grown in the Nordic countries [3, 5, 10, 18], while somewhat higher SS and pH and lower TA have been found in other studies [4, 16, 19]. The variation is certainly affected by cultivar, but chemical composition and especially sugars and acids are shown also to vary considerably with maturity, cultivation site and climate [3, 19].

3.3 Total monomeric anthocyanins and colour

Total monomeric anthocyanins (TMA) varied from 34.5 mg/100 g in 'Glen Ample' to 70.8 mg/100 g in 'Veten' (Table 4), which is somewhat higher than previous determined in the same cultivars [2, 3]. Colour was measured both on whole berries in a punnet and in mash of the berries. Chroma-values were similar for whole berries and berry mash, while L*-values were higher and Hue-values were lower in the mash compared with the whole berries, i.e. the berry mash had lighter and more bluish colour than the whole berries.

3.4 Volatile compounds

More than 100 volatile compounds were detected in the samples, but many compounds were only present in some sample parallels. Based on abundance and/or because they previously were designated as important aroma compounds in raspberries, 24 compounds were identified and quantified relative to an internal standard (Fig. 2). Identification of the volatile compounds were based on comparison with authentic standards, except for an isomer of β-ionone, (*E*)-4-oxo-2-hexenal and (*E*)-3-hexenal, which were identified based on mass spectra match with a mass spectral library. The two latter, together with (*E,E*)-2,4-hexadienal, are, to our knowledge, not previously reported in raspberries [8].

In accordance with previous studies [8], terpenes were the largest class of volatile compounds in the raspberry gentoypes. Seven monoterpenes, one sesquiterpene (β-caryophyllene) and three C13 norisoprenoids (α-ionone and two isomers of β-ionone) were quantified. The monoterpenes α-pinene and α-phellandrene were present in the highest relative concentrations in most samples. The important character impact compounds α- and β-ionone were detected in all raspberry genotypes, with the highest concentrations in 'Tulameen', 'Glen Fyne' and RU044 03090. The concentration of total terpenes plus C13 norisoprenoids, varied considerably, from about 20 ng/(g x L) in 'Glen Ample' and 'Veten' to more than 250 ng/(g x L) in 'Glen Carron' (Fig. 2A). The four esters identified were derivates of acetic acid. Ethyl acetate was the single most abundant compound in the samples, with the highest concentrations in 'Veten' and RU044 03090 (Fig. 2B). Ethyl acetate has also previously been found to be the major compound in ripe raspberries [12, 13]. 'Tulameen', together with 'Ninni', had the highest levels of C6 aldehydes and alcohols, mainly hexanal, (*Z*)-3-hexenal, (*Z*)-3-hexen-1-ol and (*E*)-4-oxo-2-hexenal (Fig. 2C). This is in accordance with previous studies, showing high concentrations of these compounds in 'Tulameen' compared with other cultivars [13, 20]. C6 aldehydes and alcohols are degradation products after oxidation of fatty acids primarily linolenic acid (C18:3, n-3) and are produced in response to stress, e.g after damage of cell structure when cutting or homogenising the berries [9]. The production of these oxidation products is dependent on enzyme activities, pH and fatty acid composition in the cell walls. Interestingly, 'Glen Carron', which contained high levels of terpenes, hardly contained any (*Z*)-3-hexen-1-ol or C6 aldehydes, which indicates that this genotype lack the precursor (C18:3, n-3) and/or the enzymes in the lipoxygenase pathway necessary to produce these compounds. Monoterpenes, the dominating volatile compounds in 'Glen Carron', on the other hand, are mainly formed by anabolic processes and are normally not altered by tissue distruption [9].

There were high correlations ($r > 0.94$, $p < 0.005$) between the various monoterpenes in the raspberry samples (Supplementary information, Table 1), except for β-myrcene, which is an acyclic monoterpene synthesised directly from geranyl pyrophosphate [21]. The sesquiterpene β-caryophyllene did not correlate with any of the other terpenes, neither did the C13 norisoprenoids, which are oxidation products of carotenoids and occur, as fatty acid oxidation, when the plant tissue is damaged. There were positive correlations ($r > 0.76$, $p < 0.05$) between all C6 compounds, but no correlation between C6 compounds and terpenes or esters, except a negative correlation with methyl acetate. Branched compounds such as 3-methylbutanal and 3-methyl-2-butenyl acetate found in 'Veten' and 'Glen Carron', respectively, are formed during the amino acid catabolism [9].

Condition of the berries, i.e. whole or homogenized, fresh or frozen, as well as sample preparation technique, is decisive for which volatile compounds are present and detected from the samples. Various sample preparation techniques have been used to determine volatile compounds in raspberries, e.g. solvent extraction [10, 22], dynamic headspace (purge and trap) [4, 12], solid phase micro-extraction (SPME) [7, 13, 14], stir bar sorptive extraction [15, 23] and proton-transfer reaction-mass spectrometry (PTR-MS) [13]. Like in other studies not using solvent extraction to extract volatile compounds in raspberries [4, 12, 13, 15], raspberry ketone was not detected in the current study. Homogenisation or processing in other ways prior to collecting volatile compounds will cause higher concentrations of fatty acid oxidation products, i.e. C6 aldehydes and alcohols. In online experiments (PTR-MS) a tremendous (150 times) increase in C6 volatiles after crushing raspberries was found, while compounds originating from plant metabolism e.g. acetate esters only increased 4-5 times [13]. We chose mild conditions for collection of volatile compounds; that is the berries were cut in halves and volatiles were collected at room temperature. This is not a quantitative method, but in line with the aim of the study, this sampling procedure is quite like what humans are exposed to when smelling the berries.

3.5 Correlation between sensory attributes and chemical variables

3.5.1 Colour

Of the instrumental measured colour parameters, L* had the highest correlation with colour attributes determined by the sensory panel (Table 5). L*, together with Chroma, correlated negatively with colour hue determined by the sensory panel and positively with colour intensity and whiteness. TMA and Hue, on the other hand, correlated positively with colour hue and negatively with colour intensity and whiteness. There were higher correlations between sensory determined colour and L* and Chroma measured on the mash than measured on the whole berries, while Hue determined on the whole berries correlated better with sensory determined attributes than hue determined on berry mash.

Sensory determined colour was assessed by the Natural Colour System (NCS), so it might be expected that high correlations were found between sensory and instrumental determined colour.

3.5.2 Odour and flavour

Multivariate regression analysis (PLS) was performed to explain the relations between chemical variables (pH, SS, TA, SS/TA and volatile compounds) (X) and odour and flavour attributes determined by the sensory panel (Y). Scores and loading plots of principal components (PCs) 1 and 2 are shown in Fig. 3. The first two PCs explained 58 and 84% of the variance in the X and Y data, respectively. The scores plot (Fig. 3A) is quite like the scores plot obtained after PCA of sensory attributes alone (Fig. 1A). The relationships between sensory attributes and chemical constituents are illustrated in the correlation loadings plot (Fig. 3B). Variables close in the diagram had the highest correlations, e.g. acidic taste and astringency had the highest association with TA, and green odour and flavour correlated best with C6 aldehydes and alcohols.

The perceived odour and flavour are the result of a mixture of volatile compounds [24], thus a single volatile compound is not expected to explain one sensory attribute. Furthermore, the odour characteristic of a compound may change with concentration [25]. Multivariate analysis may thus be expected to be suited to explain the relationship between volatile compounds and sensory attributes. In the current study, only eight samples were used in the model. More samples are needed to validate the model properly, but Fig. 3 gives an overview of the relations between sensory attributes and chemical constituent. It would be advantageous if sensory attributes could be determined by a single or a few chemical constituents, preferably easy to measure. Univariate correlation analysis was performed between sensory attributes and simple physio-chemical measurements (SS, TA and pH) and representative volatile compounds (Table 6). The volatile compounds were selected based on their internal correlation (see section 2.4). Significant ($p < 0.05$) univariate correlations were found between TA and acidic taste, astringency and flavour intensity (r > 0.75). Of the other physio-chemical measurements, SS was only correlated with watery flavour (r = - 0.77), while pH was not correlated with any of the sensory attributes. SS/TA was significant positively correlated with sour flavour (r = 0.73) and sweet taste (r = 0.85) and negatively correlated with acidic taste (r = - 0.91) and astringency (r = -0.94). There were no correlations between SS, TA or SS/TA and any of the odour attributes. Shamaila et al. [4] also found positive correlations between TA and sourness and astringency and positive correlation between SS/TA and sweetness and negative correlations between SS/TA and sourness and astringency. In addition, SS was found to correlate positively with fruitiness, sweetness and overall impression and negatively with sourness and astringency. In another study, sucrose, but not fructose or glucose, were found to correlate positively with sweetness, but there were no correlation between individual sugars and SS [5]. Furthermore, TA correlated positively with citric and malic acid, but no correlation between citric or malic acid and sensory scores for acidity was found. In a study of five raspberry cultivars, berries with high contents of soluble solids and high pH were shown to be preferred for flavour [16]. From ours and other studies, it seems that SS, TA and their ratio provide a good measure of sweet and acidic taste and astringency of raspberries. Furthermore, these sensory attributes are closely correlated with attractiveness of the berries.

Hexanal, (*Z*)-3-hexenal, (*E*)-2-hexenal and (*Z*)-3-hexen-1-ol correlated positively with green flavour (r > 0.71) (Table 6). (*Z*)-3-hexen-1-ol was also correlated with green odour. This is in accordance with the odour description of these compounds; green/herbaceous/leafy [26]. In accordance with their odour characterization “violet” and “floral” [22, 27], the two β-ionone isomers correlated with flower odour, while α-ionone was correlated with flower flavour. β-ionone has low odour threshold value and might be important for raspberry aroma [27], but the differences between humans in sensitivity for β-ionone have been found to be large (100-fold) and sensitive and less sensitive individuals perceived the odour of β-ionone differently, i.e. fragrant and floral versus sour, acidic and pungent [25]. In the present study, no correlations were found between the cyclic monoterpenes and sensory attributes. The reason could be that the descriptions used for these compounds, i.e. pine, spicy, fresh, citrus, peppery etc. for α-pinene and α-phellandrene [22, 26], were not among the sensory attributes quantified in the study. Ethyl acetate has an ether-like, bittersweet odour (nail polish remover) and a relation with chemical odour and flavour might be anticipated. This was, however, not the case, though a tendency towards correlation with cloying odour (r = 0.64, p = 0.09) was observed. Ethyl acetate had the highest peak area in most samples, however, due to high odour threshold value, its importance for odour of raspberries is found to be low [22]. The results of a study where selected aroma compounds in (previously) frozen raspberries and degree of raspberry flavour in raspberry jam were compared, indicated that raspberry ketone and α- and β-ionone were the most important aroma compounds in raspberries [10]. How the raspberry flavour was perceived by the sensory panel was, however, dependent on interaction between the volatile compounds present. Collection of volatile compounds from whole berries at higher temperature for a longer time (45 °C for 2 hours) gave different composition of volatile compounds than in our study and no correlation between volatile compounds and sensory attributes [4].

4. Conclusion

The sensory profiles of eight raspberry genotypes were discriminated by variation in firmness, sour and green flavours and odours versus chemical and cloying odours and flavours, and sweet taste versus acidic taste and astringency. ‘Ninni’, described as firm, sweet and sour with low intensities of astringency and cloying and chemical flavours and odours, might be the most attractive cultivar for the consumers.

Contents of sugars and acids, determined by simple measurements of TA and SS, and especially the SS/TA ratio, correlated well with important sensory attributes such as sweet taste, acidic taste and astringency. No correlations were found between the measured sensory attributes and terpenes, the main group of volatile compounds in raspberries. β-ionone correlated with flower odour, while α-ionone was positively correlated with flower flavour. C6 aldehydes and (*Z*)-3-hexen-1-ol correlated with green flavour. TMA correlated with colour of raspberries determined by the sensory panel. L* seemed to be the instrumental colour parameter that best could predict colour as it is observed by humans.

Simple measurement of TA and SS and their ratio, provide information about sweetness, acidity and astringency of raspberries. The gentle dynamic headspace technique used to collect volatile compounds in the study, provided additional information about flavour and odour of the berries. The established relationship between sensory attributes and instrumental measured quality, can be used in for example raspberry breeding to identify molecular markers (eg. SNPs) for important quality parameters.

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Conflict of Interest

The authors have no conflict of interest to report.

References

[1] Villamor RR, Daniels CH, Moore PP, Ross CF. Preference mapping of frozen and fresh raspberries. Journal of Food Science. 2013;78(6):S911-S9. doi: 10.1111/1750-3841.12125.

[2] Mazur SP, Nes A, Wold A-B, Remberg SF, Aaby K. Quality and chemical composition of ten red raspberry (*Rubus idaeus* L.) genotypes during three harvest seasons. Food Chem. 2014;160(0):233-40. doi: http://dx.doi.org/10.1016/j.foodchem.2014.02.174.

[3] Remberg SF, Sønsteby A, Aaby K, Heide OM. Influence of postflowering temperature on fruit size and chemical composition of Glen Ample raspberry (*Rubus idaeus* L.). Journal of Agricultural and Food Chemistry. 2010;58(16):9120-8. doi:

[4] Shamaila M, Skura B, Daubeny H, Anderson A. Sensory, chemical and gas chromatographic evaluation of 5 raspberry cultivars. Food Research International. 1993;26(6):443-9. doi: 10.1016/0963-9969(93)90090-6.

[5] Stavang JA, Freitag S, Foito A, Verrall S, Heide OM, Stewart D, et al. Raspberry fruit quality changes during ripening and storage as assessed by colour, sensory evaluation and chemical analyses. Sci Hortic-Amsterdam. 2015;195:216-25. doi: 10.1016/j.scienta.2015.08.045.

[6] Lesschaeve I, Noble AC. Polyphenols: factors influencing their sensory properties and their effects on food and beverage preferences. American Journal of Clinical Nutrition. 2005;81(1):330S-5S. doi:

[7] Forney CF, Jamieson AR, Pennell KDM, Jordan MA, Fillmore SAE. Relationships between fruit composition and storage life in air or controlled atmosphere of red raspberry. Postharvest Biology and Technology. 2015;110:121-30. doi: 10.1016/j.postharvbio.2015.07.017.

[8] Aprea E, Biasioli F, Gasperi F. Volatile compounds of raspberry fruit: from analytical methods to biological role and sensory impact. Molecules. 2015;20(2):2445-74. doi: 10.3390/molecules20022445.

[9] Christensen LP, Edelenbos M, Kreutzmann S. 7 Fruits and vegetables of moderate climate. In: Berger RG, editor. Flavours and fragrances Chemistry, bioprocessing and sustainability. Heidelberg: Springer; 2007. p. 135-88.

[10] Larsen M, Poll L, Callesen O, Lewis M. Relations between the content of aroma compounds and the sensory evaluation of 10 raspberry varieties (*Rubus idaeus* L). Acta Agriculturae Scandinavica. 1991;41(4):447-54. doi: 10.1080/00015129109439927.

[11] Vrhovsek U, Lotti C, Masuero D, Carlin S, Weingart G, Mattivi F. Quantitative metabolic profiling of grape, apple and raspberry volatile compounds (VOCs) using a GC/MS/MS method. Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences. 2014;966:132-9. doi: 10.1016/j.jchromb.2014.01.009.

[12] Robertson GW, Griffiths DW, Woodford JAT, Birch ANE. Changes in the chemical composition of volatiles released by the flowers and fruits of the red raspberry (*Rubus idaeus*) cultivar Glen Prosen. Phytochemistry. 1995;38(5):1175-9. doi: 10.1016/0031-9422(94)00782-o.

[13] Aprea E, Biasioli F, Carlin S, Endrizzi I, Gasperi F. Investigation of volatile compounds in two raspberry cultivars by two headspace techniques: Solid-Phase Microextraction/Gas Chromatography-Mass Spectrometry (SPME/GC-MS) and Proton-Transfer Reaction-Mass Spectrometry (PTR-MS). Journal of Agricultural and Food Chemistry. 2009;57(10):4011-8. doi: 10.1021/jf803998c.

[14] de Ancos B, Ibanez E, Reglero G, Cano MP. Frozen storage effects on anthocyanins and volatile compounds of raspberry fruit. Journal of Agricultural and Food Chemistry. 2000;48(3):873-9. doi: 10.1021/jf990747c.

[15] Malowicki SMA, Martin R, Qian MC. Volatile composition in raspberry cultivars grown in the Pacific northwest determined by stir bar sorptive extraction-gas chromatography-mass spectrometry. Journal of Agricultural and Food Chemistry. 2008;56(11):4128-33. doi: 10.1021/jf073489p.

[16] Bushway AA, Bushway RJ, True RH, Work TM, Bergeron D, Handley DT, et al. Comparison of the physical, chemical and sensory characteristics of 5 raspberry cultivars evaluated fresh and frozen. Fruit Varieties Journal. 1992;46(4):229-34. doi:

[17] Giusti MM, Wrolstad RE. Characterization and measurement of anthocyanins by UV-visible spectroscopy. In: Wrolstad RE, editor. Current Protocols in Food Analytical Chemistry. New York: John Wiley & Sons, Inc.; 2001. p. Unit F1.2.1-F.2.13.

[18] Skrede G, Martinsen BK, Wold AB, Birkeland SE, Aaby K. Variation in quality parameters between and within 14 Nordic tree fruit and berry species. Acta Agr Scand B-S P. 2012;62(3):193-208. doi: Doi 10.1080/09064710.2011.598543.

[19] Malowicki SMM, Martin R, Qian MC. Comparison of sugar, acids, and volatile composition in raspberry bushy dwarf virus-resistant transgenic raspberries and the wild type 'Meeker' (*Rubus idaeus* L.). Journal of Agricultural and Food Chemistry. 2008;56(15):6648-55. doi: 10.1021/jf800253e.

[20] Aprea E, Carlin S, Giongo L, Grisenti M, Gasperi F. Characterization of 14 raspberry cultivars by solid-phase microextraction and relationship with gray mold susceptibility. Journal of Agricultural and Food Chemistry. 2010;58(2):1100-5. doi: 10.1021/jf902603f.

[21] Torssell KBG. Chapter 5 The mevalonic acid pathway. The terpenes. In: Torssell KBG, editor. Natural product chemistry A mechanistic and biosynthetic approach to secondary metabolism. Chichester: John Wiley & sons limited; 1989. p. 167-225.

[22] Klesk K, Qian M, Martin RR. Aroma extract dilution analysis of cv. Meeker (*Rubus idaeus* L.) red raspberries from Oregon and Washington. Journal of Agricultural and Food Chemistry. 2004;52(16):5155-61. doi: 10.1021/jf0498721.

[23] Morales ML, Callejon RM, Ubedaab C, Guerreiro A, Gago C, Miguel MG, et al. Effect of storage time at low temperature on the volatile compound composition of Sevillana and Maravilla raspberries. Postharvest Biology and Technology. 2014;96:128-34. doi: 10.1016/j.postharvbio.2014.05.013.

[24] Le Berre E, Beno N, Ishii A, Chabanet C, Etievant P, Thomas-Danguin T. Just noticeable differences in component concentrations modify the odor quality of a blending mixture. Chemical Senses. 2008;33(4):389-95. doi: 10.1093/chemse/bjn006.

[25] Jaeger SR, McRae JF, Bava CM, Beresford MK, Hunter D, Jia YL, et al. A Mendelian trait for olfactory sensitivity affects odor experience and food selection. Current Biology. 2013;23(16):1601-5. doi: 10.1016/j.cub.2013.07.030.

[26] Burdock GA, editor. Fenaroli's handbook of flavor ingredients. 3rd ed. Boca Raton, US: CRC Press; 1995.

[27] Larsen M, Poll L. Odour thresholds of some important aroma componds in raspberries. Zeitschrift Fur Lebensmittel-Untersuchung Und-Forschung. 1990;191(2):129-31. doi: 10.1007/bf01202638.

Table 1. Parentage and origin of the raspberry genotypes

Genotype	Parentage	Origin
'Anitra'[a]	N91-63-1 x N92-68-3	Graminor Breeding Ltd., Norway, 2015
'Glen Ample'	Complex parentage	James Hutton Institute, UK, 1994
'Glen Carron'[b]	SCRI 0030E-12 x SCRI 0039F-2	James Hutton Institute, UK, 2018
'Glen Fyne'	SCRI 8631D-1 x SCRI 8605C-2	James Hutton Institute, UK, 2008
'Ninni'[c]	'Varnes' x RU004 03067	Graminor Breeding Ltd., Norway, 2015
'Tulameen'	'Nootka' x 'Glen Prosen'	Agric. Canada Research Station, Canada, 1989
'Veten'	'Preussen' x 'Lloyd George'	Graminor Breeding Ltd., Norway, 1961
RU044 03090	'Varnes' x RU004 03067	Graminor Breeding Ltd., Norway

[a] Selection RU974 07002. [b] Selection 0485K-1. [c] Selection RU044 03073.

Table 2. Definition of sensory attributes used in sensory profiling of raspberries

Attribute	Description
Colour	
Colour hue	Colour assessed on whole berries according to the Natural Colour System (NCS); No intensity = Y90R (yellowish red), high intensity = R10B (reddish blue)
Colour intensity	Colour intensity of whole berries according to NCS
Whiteness	Colour assessed on whole berries according to NCS
Odour	
Odour intensity	Intensity of all odours in the sample
Sour odour	Related to a fresh, balanced odour due to the presence of organic acids
Green odour	Associated with odour of freshly cut green grass
Flower odour	Associated with odour of flowers, perfume, honey
Cloying odour	Associated with an unfresh, sickening odour
Chemical odour	Odour of chemicals (ethyl acetate, plastic, sulphur, spirits)
Flavour/taste	
Flavour intensity	Intensity of all flavours in the sample
Sour flavour	Associated with a fresh, balanced flavour due to the presence of organic acids
Sweet taste	Related to the basic taste sweet (sucrose)
Acidic taste	Related to the basic taste acid (citric acid)
Bitter taste	Related to the basic taste bitter (quinine or caffeine)
Watery flavour	Associated with watery taste, tame, tasteless
Green flavour	Associated with flavour of freshly cut green grass
Flower flavour	Associated with flavour of flowers, perfume, honey
Cloying flavour	Associated with an unfresh, sickening flavour
Chemical flavour	Flavour of chemicals (ethyl acetate, plastic, sulphur, spirits)
Texture	
Firmness	Mechanical textural attribute relating to the force required to achieve a given deformation or penetration of a product
Juiciness	Perception of water after 3-4 chews, mouthfeel
Astringency	Organoleptic attribute of pure substances or mixtures which produces the astringent sensation

Table 3. Mean values for the 22 sensory attributes evaluated in eight raspberry genotypes[a]

	'Anitra'	'Glen Ample'	‘Glen Carron’	'Glen Fyne'	'Ninni'	'Tulameen'	'Veten'	RU044 03090
Colour								
Colour hue	6.4ab	5.1b	5.8ab	6.4ab	6.9a	6.2ab	6.9a	6.0ab
Colour intensity	6.1ab	6.4a	6.4a	6.1ab	5.9ab	6.1ab	5.6b	6.3ab
Whiteness	3.0ab	3.4a	3.3a	2.9ab	2.7b	2.9ab	2.5b	3.0ab
Odour								
Odour intensity	4.7b	5.3b	6.6a	5.2b	4.7b	5.3b	6.9a	5.1b
Sour odour	3.8abc	4.5a	2.8bc	4.3ab	4.2ab	3.9abc	2.3c	4.0ab
Green odour	2.7a	2.7a	1.5bc	2.3abc	2.7a	2.5ab	1.3c	3.1a
Flower odour	2.4a	2.6a	3.2a	3.2a	2.9a	3.0a	2.5a	2.7a
Cloying odour	2.0bc	2.1bc	3.8ab	1.7c	1.9c	1.7c	5.5a	2.3bc
Chemical odour	2.0b	2.0b	4.7a	1.6b	1.5b	1.9b	4.8a	2.1b
Flavour/taste								
Flavour intensity	6.0a	6.0a	6.3a	6.0a	5.9a	6.8a	6.7a	6.1a
Sour flavour	3.4bcd	4.2abcd	2.9de	4.5ab	5.2a	3.0cd	1.7e	4.3abc
Sweet taste	3.4c	3.6bc	4.1abc	4.4ab	4.6a	3.3c	3.3c	4.1abc
Acidic taste	6.0b	6.4ab	5.8bc	5.1cd	4.9d	7.0a	6.2b	5.7bc
Bitter taste	4.7abc	4.3abc	4.9ab	4.0c	4.1bc	4.7abc	5.2a	4.1bc
Watery flavour	2.5ab	2.5ab	2.2ab	1.8ab	1.7ab	2.1ab	3.0a	1.5b
Green flavour	3.5a	3.4a	2.6ab	2.6ab	3.8a	3.8a	2.0b	3.9a

Flower flavour	2.1ab	2.7a	2.8a	3.1a	2.7a	1.9ab	1.4b	2.5ab
Cloying flavour	2.8bc	1.8c	4.1b	2.5bc	1.8c	3.0bc	6.1a	2.5bc
Chemical flavour	2.6bc	1.9c	4.3ab	1.7c	1.6c	2.7bc	5.0a	1.8c
Texture								
Firmness	4.7ab	4.5b	4.8ab	4.6ab	5.6a	4.5b	2.8c	5.4ab
Juiceness	5.8b	6.4ab	5.8b	6.0b	5.6b	6.2ab	6.8a	5.9b
Astringency	4.7abc	5.2ab	4.8abc	4.0cd	3.7d	5.5a	4.8abc	4.3bcd

[a] The mean of 20 assessments (2 x 10 panellists). Values in a row with different letters are significant different ($p < 0.05$) based on Tukey's multiple comparisons test.

Table 4. Berry weight, pH, soluble solids (SS), titratable acidity (TA), total monomeric anthocyanins (TMA) and colour (L*, Chroma and Hue) of eight red raspberry genotypes[a]

	'Anitra'	'Glen Ample'	‘Glen Carron’	'Glen Fyne'	'Ninni'	'Tulameen'	'Veten'	RU044 03090
Berry weight (g)	6.4 ± 0.8	5.8 ± 0.5	5.5 ± 0.2	5.1 ± 0.3	6.1 ± 0.3	4.9 ± 0.9	3.8 ± 0.2	6.2 ± 0.2
pH	2.89 ± 0.01	2.96 ± 0.02	2.88 ± 0.01	2.90 ± 0.01	3.02 ± 0.01	2.79 ± 0.02	2.93 ± 0.01	2.84 ± 0.01
SS (%)	8.5 ± 0.1	8.2 ± 0.1	8.8 ± 0.3	9.3 ± 0.3	9.7 ± 0.1	9.8 ± 0.7	8.8 ± 0.0	10.2 ± 0.2
TA (%)	2.08 ± 0.05	1.97 ± 0.04	2.16 ± 0.01	1.93 ± 0.03	1.77 ± 0.02	2.80 ± 0.11	2.11 ± 0.01	2.07 ± 0.10
SS/TA	4.1 ± 0.2	4.2 ± 0.1	4.1 ± 0.1	4.8 ± 0.1	5.5 ± 0.1	3.5 ± 0.1	4.2 ± 0.0	4.9 ± 0.1
TMA (mg/100 g)	50.7 ± 1.6	34.5 ± 0.8	41.0 ± 1.3	47.4 ± 0.7	46.7 ± 0.4	46.5 ± 0.5	70.8 ± 12.9	37.5 ± 0.4
$L^*_{Berries}$[b]	18.8 ± 1.1	21.6 ± 0.3	21.4 ± 0.6	18.5 ± 1.4	18.8 ± 0.5	19.4 ± 0.2	17.0 ± 0.5	21.4 ± 0.2
$Chroma_{Berries}$[b]	42.1 ± 1.7	41.7 ± 0.1	39.3 ± 0.5	40.7 ± 1.1	37.6 ± 1.8	41.7 ± 0.6	34.7 ± 1.7	37.7 ± 0.2
$Hue_{Berries}$[b]	39.3 ± 2.2	31.9 ± 0.8	31.7 ± 1.6	39.7 ± 3.1	38.1 ± 1.9	37.7 ± 0.3	42.5 ± 1.2	30.4 ± 0.4
L^*_{Mash}[c]	28.5 ± 0.0	31.6 ± 0.5	31.2 ± 0.3	29.1 ± 0.2	28.5 ± 0.2	29.2 ± 0.2	27.2 ± 0.4	29.9 ± 0.1
$Chroma_{Mash}$[c]	41.4 ± 0.5	42.5 ± 0.4	42.4 ± 0.8	38.0 ± 0.1	38.4 ± 0.3	41.5 ± 0.2	32.1 ± 1.6	40.5 ± 0.2
Hue_{Mash}[c]	24.5 ± 0.0	22.2 ± 0.2	22.3 ± 0.1	22.4 ± 0.2	23.0 ± 0.3	23.3 ± 0.2	23.0 ± 0.1	22.2 ± 0.2

[a] The values are means and standard deviations of two parallels, i.e. berries from two punnets (each 300 g). [b] Colour measured on whole berries in a punnet. [c] Colour measured on berry homogenate.

Table 5. Correlations between colour determined by a sensory panel and total monomeric anthocyanins (TMA) and instrumentally determined colour (L*, Chroma and Hue)[a]

	Colour hue[b]		Colour intensity[b]		Whiteness[b]	
TMA	0.74	*	-0.90	**	-0.80	*
$L^*_{Berries}$[c]	-0.85	**	0.94	***	0.86	**
$Chroma_{Berries}$[c]	-0.56		0.59		0.65	
$Hue_{Berries}$[c]	0.77	*	-0.88	**	-0.78	*
L^*_{Mash}[d]	-0.91	***	0.93	***	0.94	***
$Chroma_{Mash}$[d]	-0.73	*	0.90	**	0.84	**
Hue_{Mash}[d]	0.44		-0.43		-0.34	

[a] Correlation coefficient, r. Significance: *, $p \leq 0.05$; **, $p \leq 0.01$; ***, $p \leq 0.001$. [b] Colour determined by the sensory panel. [c] Instrumentally measured colour on whole berries in a punnet. [d] Instrumentally measured colour on berry homogenate.

Table 6. Correlations between odour and flavour determined by the sensory panel and selected chemical variables[a]

Sensory attributes	pH	SS	TA	SS/TA	Ethyl acetate	Acetic acid	Hexanal	(*E*)-2-Hexenal	(*Z*)-3-hexen-1-ol	α-Pinene	β-Myrcene	β-Caryophyllene	trans-α-ionone	trans-β-ionone
Odour														
Odour intensity	-0.060	-0.302	0.188	-0.400	0.444	0.748 *	-0.532	-0.613	-0.789 *	0.316	-0.536	0.274	0.013	0.335
Sour odour	0.076	0.216	-0.195	0.351	-0.501	-0.797 *	0.501	0.632	0.666	-0.327	0.406	-0.194	0.222	0.003
Green odour	-0.072	0.379	-0.115	0.349	-0.191	-0.648	0.563	0.668	0.795 *	-0.397	0.428	-0.263	0.116	-0.351
Flower odour	-0.203	0.380	0.124	0.134	-0.446	-0.456	0.068	-0.075	-0.159	0.638	0.170	0.496	0.169	0.821 *
Cloying odour	0.141	-0.312	-0.030	-0.204	0.640	0.905 **	-0.506	-0.662	-0.744 *	0.173	-0.342	-0.041	-0.094	-0.070
Chemical odour	-0.026	-0.346	0.102	-0.352	0.424	0.719 *	-0.619	-0.726 *	-0.830 *	0.428	-0.495	0.214	0.075	0.197
Flavour/taste														
Flavour intensity	-0.454	0.069	0.765 *	-0.676	0.397	0.624	0.011	0.071	-0.086	-0.050	-0.574	0.586	-0.570	0.199
Sour flavour	0.367	0.333	-0.528	0.735 *	-0.381	-0.709 *	0.493	0.357	0.423	0.000	0.738 *	-0.349	0.333	-0.053
Sweet taste	0.379	0.432	-0.610	0.846 **	-0.153	-0.376	0.169	-0.213	-0.141	0.488	0.794 *	-0.265	0.308	0.171
Acidic taste	-0.570	-0.235	0.812 *	-0.911 **	0.061	0.195	-0.005	0.372	0.208	-0.306	-0.849 **	0.578	-0.182	0.152
Bitter taste	0.177	-0.449	0.439	-0.697	0.239	0.647	-0.448	-0.364	-0.452	0.162	-0.707 *	0.389	-0.229	0.038
Watery flavour	0.171	-0.768 *	0.145	-0.600	0.178	0.637	-0.429	-0.226	-0.354	-0.302	-0.670	-0.003	-0.149	-0.137
Green flavour	-0.195	0.494	0.171	0.162	-0.272	-0.659	0.712 *	0.771 *	0.834 **	-0.123	0.304	0.133	0.047	-0.191
Flower flavour	0.261	0.036	-0.512	0.508	-0.552	-0.698	-0.038	-0.135	-0.151	0.429	0.387	-0.104	0.703 *	0.468
Cloying flavour	-0.144	-0.216	0.262	-0.417	0.557	0.861 **	-0.502	-0.562	-0.601	0.104	-0.454	0.141	-0.362	-0.012
Chemical flavour	-0.129	-0.359	0.297	-0.528	0.372	0.743 *	-0.556	-0.586	-0.668	0.296	-0.588	0.305	-0.170	0.120
Astringency	-0.475	-0.386	0.749 *	-0.937 ***	-0.052	0.166	-0.102	0.277	0.067	-0.191	-0.918 ***	0.619	-0.034	0.282

[a] Correlation coefficient, r. Significance: *, $p \leq 0.05$; **, $p \leq 0.01$; ***, $p \leq 0.001$.

Figure captions

Fig. 1. Scores plot (A) and loadings plot (B) of factor 1 (PC1) and factor 2 (PC2) from principal component analysis (PCA) of the 20 significant sensory attributes (loadings) in eight raspberry genotypes (scores).

Fig. 2. Semi-quantitative amounts of volatile compounds in eight raspberry genotypes. A: terpenes and C13 norisoprenoids. B: esters and more. C: C6 aldehydes and alcohols.

Fig. 3. Scores plot (A) and loadings plot (B) of factors 1 (PC1) and 2 (PC2) from PLS regression analysis of pH, SS, TA, SS/TA and volatile compounds as X data and odour and flavour as Y data shown in red and blue in the loadings plot, respectively.

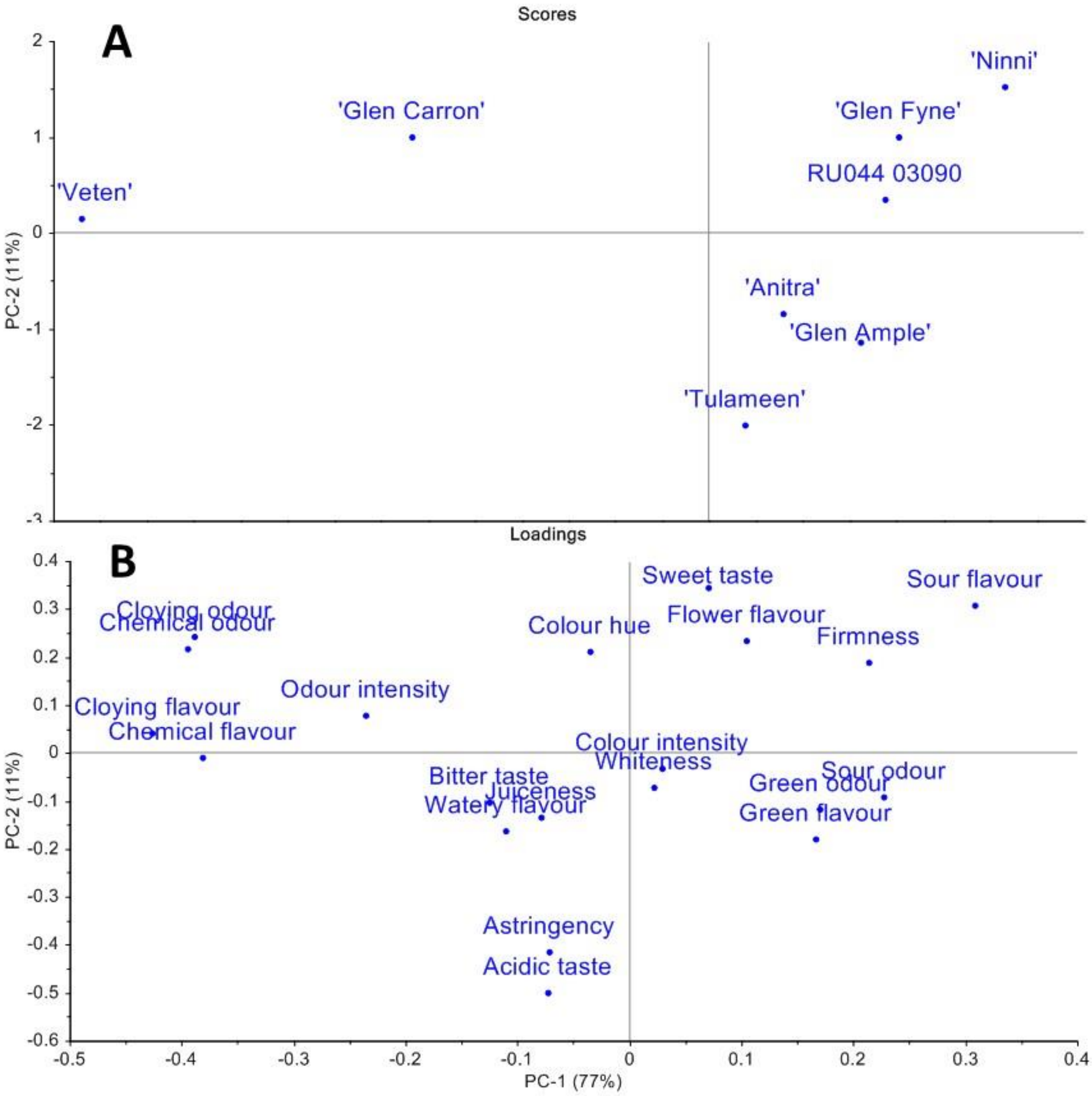
Scores
A
'Ninni'
'Glen Carron'
'Glen Fyne'
RU044 03090
'Veten'
'Anitra'
'Glen Ample'
'Tulameen'
PC-2 (11%)
2
1
0
-1
-2
-3
Loadings
B
Sweet taste
Sour flavour
Cloying odour
Chemical odour
Colour hue
Flower flavour
Firmness
Odour intensity
Cloying flavour
Chemical flavour
Colour intensity
Whiteness
Bitter taste
Juiceness
Watery flavour
Sour odour
Green odour
Green flavour
Astringency
Acidic taste
PC-2 (11%)
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
PC-1 (77%)

Fig. 1.

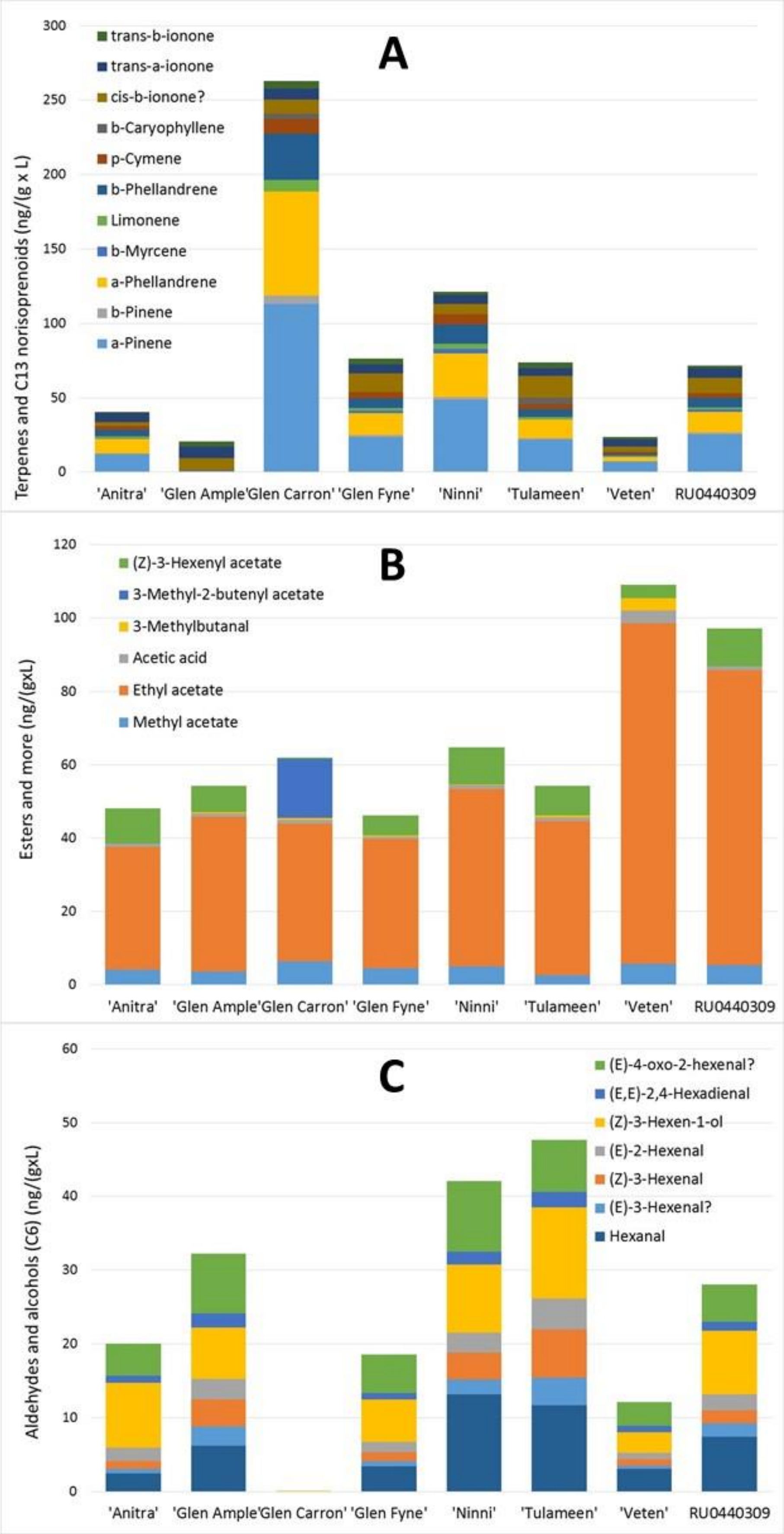
A
Terpenes and C13 norisoprenoids (ng/(g x L)
300
250
200
150
100
50
0
trans-b-ionone
trans-a-ionone
cis-b-ionone?
b-Caryophyllene
p-Cymene
b-Phellandrene
Limonene
b-Myrcene
a-Phellandrene
b-Pinene
a-Pinene
'Anitra'
'Glen Ample'
'Glen Carron'
'Glen Fyne'
'Ninni'
'Tulameen'
'Veten'
RU0440309
B
Esters and more (ng/(gxL)
120
100
80
60
40
20
0
(Z)-3-Hexenyl acetate
3-Methyl-2-butenyl acetate
3-Methylbutanal
Acetic acid
Ethyl acetate
Methyl acetate
'Anitra'
'Glen Ample'
'Glen Carron'
'Glen Fyne'
'Ninni'
'Tulameen'
'Veten'
RU0440309
C
Aldehydes and alcohols (C6) (ng/(gxL)
60
50
40
30
20
10
0
(E)-4-oxo-2-hexenal?
(E,E)-2,4-Hexadienal
(Z)-3-Hexen-1-ol
(E)-2-Hexenal
(Z)-3-Hexenal
(E)-3-Hexenal?
Hexanal
'Anitra'
'Glen Ample'
'Glen Carron'
'Glen Fyne'
'Ninni'
'Tulameen'
'Veten'
RU0440309

Fig. 2

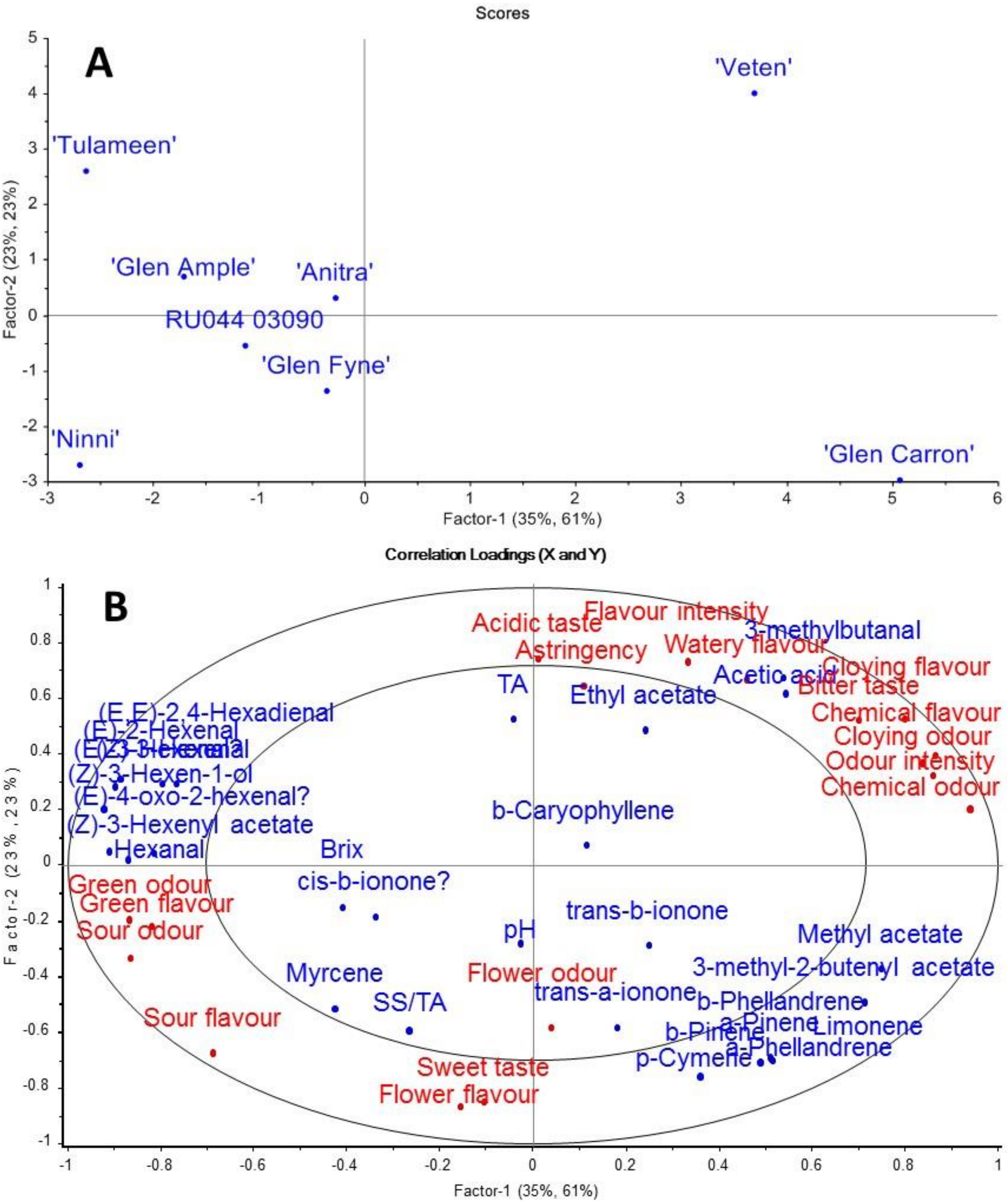
Scores
A
5
4
3
2
1
0
-1
-2
-3
Factor-2 (23%, 23%)
'Veten'
'Tulameen'
'Glen Ample'
'Anitra'
RU044 03090
'Glen Fyne'
'Ninni'
'Glen Carron'
-3
-2
-1
0
1
2
3
4
5
6
Factor-1 (35%, 61%)
Correlation Loadings (X and Y)
B
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
Factor-2 (23%, 23%)
Acidic taste
Flavour intensity
Astringency
Watery flavour
3-methylbutanal
Acetic acid
Cloying flavour
Bitter taste
TA
Ethyl acetate
Chemical flavour
Cloying odour
Odour intensity
Chemical odour
(E,E)-2,4-Hexadienal
(E)-2-Hexenal
(Z)-3-Hexen-1-ol
(E)-4-oxo-2-hexenal?
(Z)-3-Hexenyl acetate
Hexanal
Brix
b-Caryophyllene
Green odour
Green flavour
Sour odour
cis-b-ionone?
pH
trans-b-ionone
Methyl acetate
3-methyl-2-butenyl acetate
Myrcene
Flower odour
SS/TA
trans-a-ionone
b-Phellandrene
Sour flavour
b-Pinene
a-Pinene
Limonene
a-Phellandrene
p-Cymene
Sweet taste
Flower flavour
-1
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1
Factor-1 (35%, 61%)

Fig. 3

Supplementary information

Table S1. Correlations (R) between volatile compounds in the raspberry samples. Correlations of statistical significance are highlighted in yellow ($p \leq 0.05$) and pink ($p \leq 0.005$).

	Methyl acetate	Ethyl acetate	Acetic acid	3-methylbutanal	3-Methyl-2-butenyl acetate	(*Z*)-3-Hexenyl acetate	Others	Hexanal	(*E*)-3-Hexenal?	(Z)-3-Hexenal	(*E*)-2-Hexenal	(*Z*)-3-Hexen-1-ol	(*E,E*)-2,4-Hexadienal	(*E*)-4-oxo-2-hexenal?	Total C6	a-Pinene	b-Pinene	a-Phellandrene	b-Myrcene	Limonene	b-Phellandrene	p-Cymene	b-Caryophyllene	cis-b-ionone?	trans-a-ionone	trans-b-ionone
Methyl acetate		0.441	0.448	0.319	0.559	-0.491	0.569	-0.490	-0.785	-0.802	-0.854	-0.784	-0.779	-0.626	-0.737	0.574	0.572	0.560	0.211	0.554	0.567	0.524	-0.273	-0.393	0.276	-0.066
Ethyl acetate	0.441		0.814	0.680	-0.253	0.007	0.983	0.045	-0.096	-0.171	-0.168	-0.158	-0.056	-0.121	-0.096	-0.271	-0.265	-0.311	0.100	-0.312	-0.308	-0.315	-0.331	-0.302	-0.309	-0.485
Acetic acid	0.448	0.814		0.967	-0.059	-0.381	0.816	-0.209	-0.289	-0.267	-0.362	-0.438	-0.226	-0.302	-0.328	-0.182	-0.183	-0.207	-0.202	-0.210	-0.204	-0.259	-0.179	-0.489	-0.379	-0.313
3-methylbutanal	0.319	0.680	0.967		-0.068	-0.467	0.666	-0.226	-0.261	-0.198	-0.326	-0.428	-0.206	-0.293	-0.313	-0.205	-0.207	-0.226	-0.281	-0.229	-0.224	-0.269	-0.077	-0.392	-0.473	-0.180
3-Methyl-2-butenyl acet	0.559	-0.253	-0.059	-0.068		-0.742	-0.086	-0.519	-0.478	-0.446	-0.617	-0.702	-0.700	-0.718	-0.646	0.916	0.925	0.921	-0.334	0.903	0.921	0.770	0.511	0.093	0.511	0.633
(*Z*)-3-Hexenyl acetate	-0.491	0.007	-0.381	-0.467	-0.742		-0.087	0.684	0.556	0.489	0.714	0.880	0.697	0.743	0.764	-0.537	-0.565	-0.536	0.518	-0.511	-0.536	-0.377	-0.359	-0.027	-0.228	-0.641
Total Others	0.569	0.983	0.816	0.666	-0.086	-0.087		-0.026	-0.190	-0.261	-0.279	-0.269	-0.180	-0.238	-0.202	-0.103	-0.100	-0.143	0.082	-0.145	-0.139	-0.165	-0.271	-0.329	-0.228	-0.430
Hexanal	-0.490	0.045	-0.209	-0.226	-0.519	0.684	-0.026		0.832	0.848	0.851	0.785	0.852	0.852	0.943	-0.239	-0.244	-0.265	0.482	-0.229	-0.268	-0.093	0.108	0.357	-0.364	-0.192
(*E*)-3-Hexenal?	-0.785	-0.096	-0.289	-0.261	-0.478	0.556	-0.190	0.832		0.975	0.961	0.800	0.930	0.761	0.924	-0.389	-0.370	-0.407	-0.015	-0.392	-0.413	-0.364	0.356	0.506	-0.209	0.053
(Z)-3-Hexenal	-0.802	-0.171	-0.267	-0.198	-0.446	0.489	-0.261	0.848	0.975		0.953	0.786	0.907	0.754	0.923	-0.332	-0.323	-0.347	-0.008	-0.326	-0.354	-0.277	0.431	0.509	-0.332	0.099
(*E*)-2-Hexenal	-0.854	-0.168	-0.362	-0.326	-0.617	0.714	-0.279	0.851	0.961	0.953		0.923	0.954	0.830	0.971	-0.492	-0.492	-0.500	0.097	-0.479	-0.506	-0.408	0.226	0.398	-0.320	-0.119
(*Z*)-3-Hexen-1-ol	-0.784	-0.158	-0.438	-0.428	-0.702	0.880	-0.269	0.785	0.800	0.786	0.923		0.831	0.760	0.910	-0.523	-0.549	-0.522	0.268	-0.498	-0.527	-0.377	0.050	0.284	-0.419	-0.341
(*E,E*)-2,4-Hexadienal	-0.779	-0.056	-0.226	-0.206	-0.700	0.697	-0.180	0.852	0.930	0.907	0.954	0.831		0.923	0.956	-0.591	-0.577	-0.604	0.158	-0.582	-0.608	-0.517	0.031	0.261	-0.246	-0.203
(*E*)-4-oxo-2-hexenal?	-0.626	-0.121	-0.302	-0.293	-0.718	0.743	-0.238	0.852	0.761	0.754	0.830	0.760	0.923		0.905	-0.520	-0.509	-0.530	0.471	-0.500	-0.531	-0.374	-0.221	0.175	-0.176	-0.279
Total C6	-0.737	-0.096	-0.328	-0.313	-0.646	0.764	-0.202	0.943	0.924	0.923	0.971	0.910	0.956	0.905		-0.443	-0.446	-0.457	0.312	-0.428	-0.462	-0.316	0.109	0.364	-0.344	-0.196
a-Pinene	0.574	-0.271	-0.182	-0.205	0.916	-0.537	-0.103	-0.239	-0.389	-0.332	-0.492	-0.523	-0.591	-0.520	-0.443		0.996	0.998	0.028	0.998	0.998	0.955	0.466	0.198	0.383	0.555
b-Pinene	0.572	-0.265	-0.183	-0.207	0.925	-0.565	-0.100	-0.244	-0.370	-0.323	-0.492	-0.549	-0.577	-0.509	-0.446	0.996		0.992	0.009	0.989	0.992	0.936	0.467	0.233	0.438	0.602
a-Phellandrene	0.560	-0.311	-0.207	-0.226	0.921	-0.536	-0.143	-0.265	-0.407	-0.347	-0.500	-0.522	-0.604	-0.530	-0.457	0.998	0.992		0.014	0.999	1.000	0.955	0.462	0.179	0.392	0.552
b-Myrcene	0.211	0.100	-0.202	-0.281	-0.334	0.518	0.082	0.482	-0.015	-0.008	0.097	0.268	0.158	0.471	0.312	0.028	0.009	0.014		0.048	0.019	0.267	-0.545	0.014	-0.130	-0.388
Limonene	0.554	-0.312	-0.210	-0.229	0.903	-0.511	-0.145	-0.229	-0.392	-0.326	-0.479	-0.498	-0.582	-0.500	-0.428	0.998	0.989	0.999	0.048		0.999	0.966	0.456	0.176	0.367	0.533
b-Phellandrene	0.567	-0.308	-0.204	-0.224	0.921	-0.536	-0.139	-0.268	-0.413	-0.354	-0.506	-0.527	-0.608	-0.531	-0.462	0.998	0.992	1.000	0.019	0.999		0.956	0.453	0.173	0.395	0.548
p-Cymene	0.524	-0.315	-0.259	-0.269	0.770	-0.377	-0.165	-0.093	-0.364	-0.277	-0.408	-0.377	-0.517	-0.374	-0.316	0.955	0.936	0.955	0.267	0.966	0.956		0.368	0.219	0.222	0.448
b-Caryophyllene	-0.273	-0.331	-0.179	-0.077	0.511	-0.359	-0.271	0.108	0.356	0.431	0.226	0.050	0.031	-0.221	0.109	0.466	0.467	0.462	-0.545	0.456	0.453	0.368		0.581	-0.076	0.698
cis-b-ionone?	-0.393	-0.302	-0.489	-0.392	0.093	-0.027	-0.329	0.357	0.506	0.509	0.398	0.284	0.261	0.175	0.364	0.198	0.233	0.179	0.014	0.176	0.173	0.219	0.581		-0.004	0.706
trans-a-ionone	0.276	-0.309	-0.379	-0.473	0.511	-0.228	-0.228	-0.364	-0.209	-0.332	-0.320	-0.419	-0.246	-0.176	-0.344	0.383	0.438	0.392	-0.130	0.367	0.395	0.222	-0.076	-0.004		0.353
trans-b-ionone	-0.066	-0.485	-0.313	-0.180	0.633	-0.641	-0.430	-0.192	0.053	0.099	-0.119	-0.341	-0.203	-0.279	-0.196	0.555	0.602	0.552	-0.388	0.533	0.548	0.448	0.698	0.706	0.353	
Terpenes and C13 noriso	0.517	-0.331	-0.251	-0.263	0.907	-0.518	-0.168	-0.226	-0.358	-0.299	-0.455	-0.481	-0.571	-0.503	-0.415	0.996	0.992	0.996	0.026	0.995	0.996	0.959	0.497	0.261	0.380	0.594