

Nashi or Williams pear fruits? Use of volatile organic compounds, physicochemical parameters, and sensory evaluation to understand the consumer's preference

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Abstract Ripen “ready-to-eat” fruits of “Williams” and of two Nashi cultivars (“Hosui” and “Ya Li”), present contemporarily on the stores, were evaluated by physicochemical parameters (shape, skin color, firmness, total soluble solids, titratable acidity), volatile organic compounds (VOCs) emission, measured with a proton transfer reaction-time of flight-mass spectrometer (PTR–ToF–MS), either on whole and cube fruits, and sensory evaluation (panel test and consumer's liking). The data were analyzed by ANOVA, LSD test, hierarchical clustering, PLS-DA, and CCOA. The highest differences for the physicochemical parameters were observed between Williams and Nashi, as Williams differentiated for sugar content and Hosui for firmness. By VOCs spectral analyses, it was observed that whole and cube “Williams” fruits had the highest number and amount of compounds, followed by “Ya Li;” “Hosui” was characterized by a few signals with low intensities. Fruits of each cultivar showed specific VOCs that could be used as markers for discrimination purposes. In “Williams” pears, the presence and amount of defined masses resulted linked to fruitiness and aroma perceived by the consumer. The higher sugar content and the typical pear aroma perceived by the panelists, emitted by “Williams,” could have influenced the consumer's liking. The tasters appreciated “Hosui” for

firmness, and “Ya Li” for visual, even if they resulted lower in sugar and flavor intensity. In the opinion of the respondents to the consumer test, “Williams” resulted the most appreciated both for the average scores of the acceptability and as percentage of responses at a level >5 of a nine-point hedonic scale.

Keywords Consumer acceptance · Fruit sensory attributes · Instrumental analysis · Pear aroma · PLS-DA · PTR–ToF–MS

Introduction

Pyrus, a genus of Pomaceae, includes different temperate fruit tree species with major economic importance in the world market. At least 22 primary species of *Pyrus* were recognized, but only a few of them (including *Pyrus bretschneideri*, *P. pyrifolia*, and *P. communis*) have been utilized for fruits production [1] by cultivating a large number of cultivars. A general and common distinction of pear assortment is based on the geographic origin of the species, and hence, pear crop is divided into European pears (designed as “pears”) and Asian pears (known as “Nashi pears” in the Western markets). Traditionally, in Europe and namely in Italy, only the cultivars belonging to *P. communis* L. were grown to produce the typical soft and juicy dessert fruit [2], while others species, such as *P. bretschneideri* (Rehd.) and *P. pyrifolia* (Burm.) Nakai, were grown and cultivated mainly in East Asia [3], appearing on the European markets as “exotic” novelties. Today, from early autumn, fruits of cultivars belonging to different eastern pear species are present in the stores together with the “traditional” European ones. The Italian market is still dominated by a few cultivars of *P. communis*, among

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which “Williams’ Bon Cretien” pear, available from August to October on fresh market, is one of the most representative cultivars of the European pear production (65% of European production) [4], thanks to its high productivity of fruits with a typical delicious taste. In the same period of the year, crispy fruits of two “Nashi pear” cultivars, namely “Hosui” (*P. pyrifolia*), and “Ya Li” (*P. × bretschneideri*), can be found on the Italian market. Generally, the European pears are distinguished by their juiciness and pleasant flavor-aroma, while the Asian pears for their grittiness, crispness, and sweetness [5]. A few attributes are seen as the quality key indicators of pears, such as sweetness and firmness, but the main attribute that differentiates all *Pyrus* fruits species is aroma [6]. In particular, sweetness and aroma are positively correlated with the consumer’s preference [7]. The volatile compounds that contribute to fruit flavor (more than 300 volatile organic compounds, VOCs) detected in *P. communis* [8] are produced through metabolic pathways during ripening, harvest, post-harvest, and storage, and are influenced by many factors related to species, cultivar, and post-harvest treatments [9]. Following the parameters listed above, for the consumer the liking characteristics for “Williams” pears are largely identified and reported by scientific communications, whilst for the Nashi pears not exhaustive data are reported in bibliography [7].

In the last decades, gas chromatography coupled with a mass spectrometry detector (GC–MS) was the most used technique for the identification and quantification of VOCs from fruits [6]. Recently, for VOCs detection and quantification on fruit matrices, the proton transfer reaction-time of flight-mass spectrometry (PTR–ToF–MS) technology was proposed as a rapid technique, able to provide a comprehensive mass spectrum with high-time resolution, and without sample treatment [10]. This technique has been used previously on fruit samples to investigate: (a) the emission of VOCs from different fruits as strawberry [11], apple [12], olive [13], pepper [14], and mango [15]; (b) the influence of the shipping systems on the mango fruits quality [16]; (c) the VOCs emission change in postharvest decay within climacteric and perishable tropical fruits [17]; (d) the volatile fingerprints of orange juices subjected to different treatments [18]. To date, there is a considerable amount of literature about the volatile components of pear fruits; however, only a few studies on Williams and Nashi pears have investigated and related the physicochemical parameters, volatile compounds, and sensory evaluation to the consumer’s preference [7].

The aim of this research was: (1) to evaluate and compare through physicochemical parameters, volatile compounds, and sensory analysis, three different “ready to eat” cultivars of pears; (2) to identify the typical volatile markers for each pear species; (3) to identify the volatile

markers emitted by fruit which may influence the liking level of consumers, in order to better understand the preferences for these fruits.

Materials and methods

Plant material

“Ready to eat” fruits present in the Italian market during the month of October belonging to three different *Pyrus* species, namely *P. pyrifolia* cv “Hosui” (H); *P. × bretschneideri* cv “Ya Li” (Y), and *P. communis* cv “Williams” (W), were used to compare and evaluate their physicochemical, aromatic, and sensory characteristics. A set of 80 homogeneous fruits per species was acquired from a local market (Florence, Tuscany, Italy), in particular: 40 fruits for sensory analysis, 20 for physicochemical analyses and 20 for spectrophotometric analyses (PTR–ToF–MS). Fruits were stored in a climatic chamber (14 ± 1 °C, 85–90% relative humidity) for two days prior to laboratory analysis.

Physicochemical analyses

The physicochemical parameters were evaluated through the same procedure previously used in Taiti et al. [14, 16]; here below all details are reported.

Size and shape

The fruits size was evaluated with the 6.2.8 descriptor; for the shape, the cultivars were classified with the descriptor 6.2.10 [19].

Peel color

The identification of the different peel color of pear fruits was assessed using a Minolta CR-200 chromameter (Minolta, Ramsey, NJ, USA). To identify the stages of fruit ripeness, the color was determined according to the Hunter scale that utilizes three values to create a three-axis graph on which the values can be plotted [20, 21]: L^* value (lightness) varies from 100 for bright white to zero for dark black, a^* value ($+a$ is red and $-a$ is green) ranges from green to red, b^* value ($+b$ is yellow and $-b$ is blue) ranges from blue to yellow, whilst neutral gray is denoted at $a^* = 0$ and $b^* = 0$.

Firmness

Firmness (expressed as kgf) was measured as the force needed to reduce fruit diameter by 2 mm using firmness tester (Model 53205D, Turoni, Italy).

Total soluble solids (TSS)

To evaluate TSS concentration, each sample of pear fruit was cut and squeezed in order to collect few drops of juice; then TSS levels were measured with an N1 Atago refractometer (Atago Co., Japan) and expressed as °Brix.

Titrateable acidity (TA)

Titrateable acidity (TA) was measured on 15 g of pulp blended with 150 mL of distilled water; the solution was filtered, and the TA was determined by the AOAC method [22], and the results expressed as grams of malic acid/100 g of fresh weight (FW).

PTR–ToF–MS acquisition

Measurements were performed using a PTR–ToF 8000 (IONICON Analytik, GmbH, Innsbruck, Austria), which guarantees high sensitivity with a very high-time resolution and no need of sample preparation [23]. The basics of the PTR–ToF–MS technique are described elsewhere [24, 25]. This instrument is able to provide a complete and objective analyses of volatile compounds emitted by fruit samples [13, 26]. The analysis was conducted on: (1) whole fruit; (2) cubes of fruit. In the analysis of the whole fruit, peel was included, while the cube samples were obtained only from the pulp (3 × 3 × 3 cm). Twenty fruits were analyzed for each species of pear, and additional replicates were obtained. Measurements were carried out following the procedure used by Taiti et al. [16]. Each sample (whole or cube samples) was placed into a glass jar provided with two Teflon tubes (internal diameter 0.5 mm), namely the air inlet and outlet, located on opposite sides. The inlet tube was connected to a zero-air generator (Peak Scientific instruments, USA) and the outlet to the PTR–ToF–MS for dynamic headspace analysis. Glass jars of 1 L and 250 mL were used, respectively, for whole fruits and cube samples. Background was measured prior to the analysis of each fruit sample.

The following parameters were used: range mass-to-charge ratio (m/z) between 20 and 210, acquisition of one spectrum every 2 s and 60 spectra average to evaluate VOCs. Before each sample measurement, a blank sample was obtained analyzing an empty jar. The operating conditions in the drift tube were set at: applied voltage 600 V, pressure 2.25 mbar, extraction voltage at the end of the tube 35 V, thus corresponding to an E/N value of 130 Td (1 Td = 10^{-17} V cm $^{-1}$). Moreover, the temperature of both the inlet and drift tube was maintained at 60 and 40 °C, respectively, to prevent loss of the volatiles

along the inlet sampling line. The inlet flow was set at 50 sccm.

PTR–ToF–MS data analysis

Raw data were continuously acquired with the TofDaq™ software (Tofwerk AG, Switzerland). The internal calibration of mass spectral data was based on $m/z = 21.022$ (H_3O^+), $m/z = 59.049$ ($\text{C}_3\text{H}_7\text{O}^+$), and $m/z = 137.132$ ($\text{C}_{10}\text{H}_{17}^+$) and was performed off-line. The peak shape, fitting algorithms for PTR–ToF–MS spectra, acquisition of raw data, and quantification of peaks were performed according to a procedure discussed extensively in others studies [27, 28]. In the present study, the commercially available TofViewer software (version 1.4.3, Ionicon Analytik) was used for data post-processing. Peak intensity expressed in ppbv was estimated using the formula described by Lindinger et al. [29] using a constant value for the reaction rate constant coefficient ($k = 2.10 \cdot 10^{-9}$ cm 3 s $^{-1}$). Following the procedure used by Aprea et al. [26], data were filtered by eliminating peaks imputable to water chemistry (hydronium ion, water clusters) and to interfering ions (e.g., oxygen, nitrogen monoxide). Subsequently, a threshold of 1 ppbv was applied, to eliminate those signals related to ions present in trace amounts and therefore hard to quantify precisely. Thus, after filtering, a total of 54 mass spectral peaks were obtained and putatively identified.

Sensory measurements

Sample preparation

A total of 40 fruit samples for each cultivar were used for panel and consumer test. Each fruit was divided into four-slices sample and given to the panelists for sensory evaluation. Peeled slices were presented to the judges (at most 1 h after the cut, to avoid the browning process) with randomized three-digit coded samples. The order in which the samples were given to each judge was randomized. Mineral water and unsalted crackers were used for the consumers to cleanse their palates between each test. All evaluations were conducted under white illumination and at room temperature within an individual booth. Since the quality of consumer perception is influenced by intrinsic and extrinsic attributes (e.g., price, dimension, size, origin, ripening stage) [30–32], none of these attributes were mentioned to the judges.

Panel test

The sensory evaluation was performed following the procedure previously used for pear fruits [33] with some variations. Briefly, 15 pears for each cultivar were used for

sensory analysis and were presented to 15 panelists. Before starting, the method of assessment and a set of eleven descriptive attributes were selected by the judges. The panelist evaluation will cover the following attributes: aroma intensity, flavor, sweetness, juiciness, graininess, fibrousness, acidity, firmness, crunchiness, astringency, and visual appearance. Evaluation was based on a five-point scale: 1 = extremely poor; 3 = poor; 5 = acceptable (limit of marketability); 7 = good; 9 = excellent) [34], and it was preceded by a visual assessment, both on whole fruits (one per cultivar) and on peeled pieces. Trained panelists were staff members at the University of Florence (School of Agriculture) with familiarity to pears (including Nashi), frequently involved in panel tests, selected, and trained according to guidelines in ISO/DIS 8586-1 and ASTM STP 758 (1993). Indeed, the judges were recruited and selected for their ability to evaluate sensory food and for their ability to communicate their perceptions. Moreover, to make comparable the data, an analogous scale was used both for the sensory evaluation and the consumer test.

Consumer acceptability

The remaining part of fruits (25) for each cultivar was prepared for consumer test as described in “sample preparation” section. Judges, a panel of 50 women and 50 men, aged between 22 and 70 years and regular consumers of pears, were randomly selected within research staff and students at Florence University.

All the judges were Italians coming from different geographic areas. The selection comprised judges unfamiliar with these products, having no previous training in sensory evaluation work. Pears evaluation was done asking a question to the judges: “In your opinion, what is the perceived acceptability of these pears?” The acceptance of each pear has been evaluated according to a nine-point hedonic scale (1 = dislike extremely; 2 = dislike very much; 3 = dislike moderately; 4 = dislike slightly; 5 = neither like nor dislike; 6 = like slightly; 7 = like moderately; 8 = like very much; 9 = like extremely) [35]. A score of six is considered a commercial quality limit [36]. Consumer acceptance was calculated as the percentage of respondents who liked the sample, with scores >5; while consumer dislike value was calculated as the percentage with scores <5 [37].

Statistical data analyses

One-way analyses of variance (one-way ANOVA) were performed to compare the physicochemical data (Firmness, TA, TSS, Color), the sensory evaluation, and the consumer acceptability results, respectively; the separation of means was calculated by the Fisher's least significant difference (LSD) test. Computations were performed by Statgraphics

Centurion XV v. 15.0.04 and Microsoft Office Excel 2007. Furthermore, to take into account the judges, the sensory data were processed utilizing the official statistical approach adopted by the International Olive Oil Council. It was established as reliable a percentage robust coefficient of variation of the descriptors ≤ 20 (COI/T-20/Doc. no. 22-RES-2/93-IV/05).

A hierarchical clustering (unsupervised method) was performed on spectral data (average of triplicates) of 20 samples for cultivar, both whole and cube sample fruits. The group average (UPGMA) method with Euclidean distance was selected to calculate the distance among clusters, whose exact number was unknown a priori. The cophenetic correlation of the dendrogram was calculated. Computations were performed by the hierarchical clustering by distance optimization (module HIERCLUS, SYN-TAX 2000 program package) [38]. The resulting one dimensional dendrogram was represented by a heat map built up by R 3.2.2. (R Foundation for Statistical Computing, Vienna, Austria).

Multivariate partial least squares-discriminant analyses (PLS-DA) (supervised method) were applied on: a total of 120 spectra (each one comprehensive of 54 masses), 3 *Pyrus* cultivars, 60 whole fruits and 60 cube fruit samples (20 for each cultivar). This method allowed to explore the possibility to correct classify the three different cultivars of *Pyrus*, and to develop two distinct models for differentiating the three genotypes by means of whole and cube fruits, respectively. For each model, as pre-processing step, data were submitted to a logarithmic transformation and auto-scaling. The whole dataset of 60 samples was split into train and validation subsets, optimally chosen with the Euclidean distances based on the algorithm of Kennard and Stone [39]. The training set consisted of about 90% of the samples, used for selection of the optimal number of latent variables (LVs), model calibration, and cross-validation (internal validation); the test set, used to predict the class membership (external validation), included 10% of samples removed from the dataset. The training set was used to fit a model based on cross-validation procedures (venetian blinds w/7 splits and 1 samples per split), evaluated by the number of correct predictions and the root-mean-squared error of cross-validation (RMSECV), subsequently validated with the removed samples (external validation set). External validation of the model was quantified by the root-mean-squared error of prediction (RMSEP). The optimal number of LVs was selected as those associated to the minimum error and misclassification rate of the calibration dataset. Confusion matrices were used to study the reliability of the models. The threshold to assign a sample to a class was chosen minimizing the number of false positives and false negatives (Bayes theorem). Variable Importance in Projection (VIP) scores ($p = 0.01$) were also calculated. To help identify possible overfitting of the model through a

random permutation of the class labels, a permutation test (50 iterations) was also carried out, so that nonsense datasets were generated for comparison with the real model. This procedure provides a probability that the given model is significantly different from one built under the same conditions but on random data. PLS-DA analysis was performed by PLS-Toolbox v. 8.0.2 (Eigenvector Research Inc., West Eaglerock Drive, Wenatchee, WA, USA) for MATLAB® R2015b (Mathworks Inc., Natick, MA, USA).

In addition, to highlight the relationships between the VOCs emitted by pears cube sample fruits belonging to the three different cultivars and the olfactory attributes perceived by the panelists (aroma and flavor), it has been applied a variant of correspondence analysis (canonical correspondence analysis, CCOA) that allows to find the optimum fit of the two ordinations directly and simultaneously. The positions of objects and variables in their joint ordination should mutually correspond to one other. In this case, one domain is constituted by the VOCs set, whereas the constraining variables are represented by the sensory attributes; the ordination axes for the VOCs (the criterion variables) are constrained by the other set, the sensory notes (explanatory variables). To avoid the risk of misleadingly high values of VOCs/sensory notes correlation, it have been also considered the eigenvalues in evaluating the importance of ordination axes (Computations were performed by the module ORDIN, SYN-TAX 2000 program package [38]).

Results and discussion

Physicochemical fruit parameters

In Table 1, results of the analyzed physicochemical parameters are reported. Most of the physicochemical parameters showed important differences between Williams and the




two Nashi pears, and also within the Nashi cultivars. This variability could be attributed to genotype effect, alone or together with the different environmental growing conditions combined with the level of ripening at harvest, storage system, and timing to produce a ready-to-eat fruit.

The shape was rounded in “Hosui” (level 1.5 of descriptor 6.2.10 [19]), and more elongated in “Ya Li” than in “Williams” (levels 7.4 and 5.4, respectively).

Interestingly, concerning the skin color, considered a very important index for pear quality and consumer acceptance [40], strong statistical differences ($p = 0.01$) between Nashi pears and the Williams pear were identified. “Hosui” had the highest “*L*” (79.82) resulting the most brighten “Williams” showed the highest value for “*b*” (46.32 in the yellow component) and the more negative value for “*a*” (−11.92 in the green component). For the “yellow” component, “Williams” showed the highest intensity, followed by “Ya Li” and “Hosui;” the values of *a** indicated a progressive reduction of “green” color from “Williams” to “Ya Li”, the latter showing to turn to yellow.

Other physicochemical parameters, namely firmness, sugar content (TSS), and titratable acidity (TA), are very important properties because directly related to fruits eating quality [41] and correlated with consumer acceptance [42, 43]. Regarding the firmness, it directly affects the texture and edibility of fruits. The two Nashi cultivars showed statistical different values ($p = 0.01$), while no differences were found between “Hosui” and “Williams,” resulting both harder than “Ya Li.” The firmness values reported for “Ya Li” fruits were in accord with [44] that reported a great decline of this parameter during their storage. Similarly, the high firmness highlighted for “Hosui” pears confirms the peculiarity of several Asian pear cultivars that remain hard enough during the storage phases, thus avoiding transport damages [45]. Finally, it is noteworthy to observe that the “Williams” fruits showed the highest total sugar content, followed by “Hosui” and lastly “Ya Li” fruits with the

Table 1 Physicochemical parameters: fruit shape, skin color, firmness, TA, and TSS

Cultivar	Fruit shape ^a	Fruit shape ^a	Skin color			Firmness (kgf)	TA (meq/100 g)	TSS (°Brix)
			<i>L</i> *	<i>a</i> *	<i>b</i> *			
Hosui	1.5		79.82 ± 1.75 C	−5.581 ± 0.48 B	24.378 ± 3.16 A	4.02 ± 0.29 B	0.21 ± 0.03 B	12.69 ± 0.76 B
Ya Li	7.4		67.83 ± 4.55 A	−3.52 ± 1.19 C	30.71 ± 2.65 B	2.30 ± 0.38 A	0.18 ± 0.04 AB	10.8 ± 0.94 A
William	5.4		71.65 ± 2.04 B	−11.92 ± 2.06 A	46.321 ± 1.106 C	3.90 ± 0.80 B	0.17 ± 0.03 A	13.43 ± 0.67 C

Different capital letters within a column indicate differences by the LSD test at the 99.0% confidence level ($p = 0.01$)

^a Descriptor list for pear (Thibault et al. [19])

lowest values ($p = 0.01$). Accordingly, “Williams” pears showed the lowest TA and “Hosui” the highest ($p = 0.01$).

VOCs headspace analysis

Fruit aroma is one of the most important attributes to define fruit quality [46]. Along the ripening process, many VOCs are synthesized, simultaneously and involving several biosynthetic pathways; their composition and concentration are a function of the time course of the ripening [47]. Accordingly, the typical pear aroma is determined by a mix of volatile compounds, which originate during the different phases of fruit growth and are dependent on many genetic, environmental and post-harvest factors [6]. Since each VOC has a different threshold of perception, fruit aromatic fingerprint and concentration could represent a good indicator for the fruit quality and its acceptance by the consumer [47]. Table 2 shows all the putative compounds detected, along with their m/z ratio (measured), chemical name, molecular formula and the related references. The putative identification of peaks was performed on the basis of the PTR–ToF–MS characteristic high mass resolution and rapid identification of compounds with a high level of confidence [48]. Furthermore, putative compounds were also assigned by comparison with available literature on pear (or another fruit when not available) and GC–MS data and fragmentation patterns (when available). Previous works performed on different fruits had already demonstrated the possibility to establish correlations between gas-chromatographic peaks and PTR–MS mass spectral data [15, 49–52].

The heat map obtained applying hierarchical cluster analysis on the VOCs dataset is reported in Fig. 1 (different colors are related to different amounts of each detected protonated mass). The heat map highlighted six main groups, each one deriving from the combination among species and sample type (whole or cube fruits). Indeed, the VOCs signals varied consistently between (1) different pear species (*P. communis*, *P. bretschneideri*, *P. pyrifolia*) and between (2) whole and cube sample fruits, both concerning their nature and intensity (Table 2; Fig. 1). In particular, we observed that “Williams” fruits, both as whole and cube samples, had the highest number of compounds (52 and 37, respectively), with the highest amount, followed by “Ya Li” fruits that generated a great amount of signals with a concentration sometimes lower and sometimes higher than “Williams” ones (53 and 29 compounds, respectively, for whole and cube samples); “Hosui” cultivar was instead characterized by few signals with low intensities (29 and 28 compounds, respectively, for whole and cube samples) (Table 2; Fig. 1).

In pear fruits, VOCs volatile profile is mainly represented by esters, alcohols, hydrocarbons, aldehydes, and

ketones [8]. According to previous works [8, 44, 53], the following m/z detected correspond to compounds which strongly contribute to the typical pear flavor: ethyl acetate (measured m/z 89.059), ethyl 2-methylbutanoate (m/z 131.106), hexyl acetate and ethyl hexanoate (m/z 145.122), butyl acetate/ethyl butanoate (m/z 117.091), hexanal (m/z 101.060), propyl acetate/ethyl propanoate (m/z 103.075), farnesene (m/z 205.195) (Fig. 2). Curiously, highest signals intensity of certain compounds that give a typical pear aroma was detected in “Ya Li” pear, followed by “Williams” and then “Hosui”. Nevertheless, “Williams” distinguished from the other Asian cultivars for the highest intensity of signals of terpenes, sesquiterpenes and butanal.

As shown in Fig. 2 and in Table 2, the number of compounds and their amount were higher in whole fruits than in cube sample pears, probably associated to the presence of the peel. It is well known that the pericarp tissue of the peel produces a great quantity of volatile compounds [54, 55]. Accordingly, Chervin et al. [56] showed that the skin emitted most of the esters, especially ester hexanoate. Such great aroma production from the peel tissue is due to the abundance of fatty acid substrates and by the higher metabolic activity [57]; fatty acids, liberated by the lipase activity and β -oxidative enzymes and/or lipoxygenase (LOX), are generally regarded as the initial precursors of straight-chain esters, alcohols, and aldehydes produced in fruits [58]; those compounds are derived, for example, from linoleic acid and linolenic acid via lipoxygenase activity. Accordingly, a relationship between deficiency of fatty acids and poor aroma production has been observed [59].

PLS-DA approach was applied to find VOCs able to discriminate among cultivars. By applying the model developed by the PLS-DA on whole and cube sample pears data, a correct distinction of the taxonomic category of the three different *Pyrus* genotypes was achieved. Scores and Biplot of the PLS-DA model are shown in Fig. 3. In whole and cube samples, the optimal latent variables number associated to the minimum error rate (calibration and CV classification error average = 0.0000) and concurrently to the minimum number of not assigned samples (0.00) resulted in 2 LVs (Fig. 3a, b).

For both types of samples (whole and cube), the permutation test evaluated by Wilcoxon, Sign Test and R and t test indicated that the model is significant at 95% confidence level. The global quality of the model, evaluated by its performances indicators (Table 3), resulted robust to discriminate the three *Pyrus* genotypes samples in the model/validation data set, and in the independent test set. Indeed the PLS-DA three-components model successfully classified 100% of pears samples into their taxonomic category in fitting, cross-validation (internal validation), and prediction (external validation). In addition, to provide a more detailed characterization of the VOCs emitted by

Table 2 Masses found by PTR–ToF–MS

Number of compounds	Putatively identification	Mass measured	Chemical formulae	Signals presence or absence in whole fruits			Signals presence or absence in cube samples			References
				Signals presence or absence in whole fruits		Signals presence or absence in cube samples				
				Williams	Hosui	Ya Li	Williams	Hosui	Ya Li	
1	Acetylene	27.022	C ₂ H ₃ ⁺	×	×	×	×	×	×	n.a.
2	Ethylene (isotope)	30.046	C ₂ H ₆ ⁺	×	×	×	×	×	×	n.a.
3	Formaldehyde	31.018	CH ₃ O ⁺	×	×	×	×	×	×	[8]
4	Methanol	33.033	CH ₅ O ⁺	×	×	×	×	×	×	[8]
5	Isoprene fragment	39.022	C ₃ H ₃ ⁺	×	×	×	×	×	×	[51]
6	Fragment (alcohols and esters)	41.038	C ₃ H ₅ ⁺	×	×	×	×	×	×	[62]
7	Fragment (esters)	43.017	C ₂ H ₃ O ⁺	×	×	×	×	×	×	[62]
8	Fragment (alcohols)	43.054	C ₃ H ₇ ⁺	×	×	×	×	×	×	[62]
9	Acetaldehyde	45.033	C ₂ H ₅ O ⁺	×	×	×	×	×	×	[8]
10	Ethanol	47.049	C ₂ H ₇ O ⁺	×	×	×	×	×	×	[44]
11	n.a.	53.038	C ₄ H ₅ ⁺	×	×	×	×	×	×	[62]
12	n.a.	55.017	C ₃ H ₃ O ⁺	×	×	×	×	×	×	n.a.
13	C4 fragment	55.054	C ₄ H ₇ ⁺	×	×	×	×	×	×	[62]
14	Fragment (hexanal/hexyl acetate)	57.033	C ₃ H ₅ O ⁺	×	×	×	×	×	×	[62]
15	Hexanol fragment	57.069	C ₄ H ₉ ⁺	×	×	×	×	×	×	[26]
16	Acetone	59.049	C ₃ H ₇ O ⁺	×	×	×	×	×	×	[8]
17	Acetic acid/2-propanol	61.028	C ₂ H ₅ O ⁺	×	×	×	×	×	×	[44]
18	n.a.	65.038	C ₅ H ₅ ⁺	×	×	×	×	×	×	[62]
19	Terpenes fragment	67.054	C ₅ H ₇ ⁺	×	×	×	×	×	×	n.a.
20	Furan	69.033	C ₄ H ₅ O ⁺	×	×	×	×	×	×	[53]
21	Isoprene/terpenes fragments	69.069	C ₅ H ₉ ⁺	×	×	×	×	×	×	[16]
22	2-Butenal	71.049	C ₄ H ₇ O ⁺	×	×	×	×	×	×	[62]
23	2-Butanone/butanal	73.064	C ₄ H ₉ O ⁺	×	×	×	×	×	×	[8]
24	Methyl acetate	75.044	C ₃ H ₇ O ₂ ⁺	×	×	×	×	×	×	[44]
25	C6 fragment	77.038	C ₆ H ₅ ⁺	×	×	×	×	×	×	[63]
26	Fragment (xylene/ethylbenzene)	79.054	C ₆ H ₇ ⁺	×	×	×	×	×	×	[25]
27	Terpenes Fragments	81.069	C ₆ H ₉ ⁺	×	×	×	×	×	×	[51]
28	2-Methyl furan/pyran	83.049	C ₅ H ₇ O ⁺	×	×	×	×	×	×	[13]
29	C6 compounds/hexenol fragment	83.085	C ₆ H ₁₁ ⁺	×	×	×	×	×	×	[16]
30	2-Furanone	85.028	C ₄ H ₅ O ₂ ⁺	×	×	×	×	×	×	[52]
31	1-Penten-3-one	85.064	C ₅ H ₉ O ⁺	×	×	×	×	×	×	[8]
32	1-Hexanol/Nonanol	85.101	C ₆ H ₁₃ ⁺	×	×	×	×	×	×	[62]
33	2,3-Butandione	87.044	C ₄ H ₇ O ₂ ⁺	×	×	×	×	×	×	[8]

Table 2 continued

Number of compounds	Putatively identification	Mass measured	Chemical formulae	Signals presence or absence in whole fruits			Signals presence or absence in cube samples			References
				Williams		Ya Li	Williams		Ya Li	
				Hosui	Ya Li		Hosui	Ya Li		
34	Ethyl acetate/ethyl etanoate	89.059	C ₄ H ₉ O ₂ ⁺	×	×	×	×	×	[44]	
35	Terpenes fragments	93.069	C ₇ H ₉ ⁺	×	×	×	×	×	[51]	
36	Terpenes fragments	95.085	C ₇ H ₁₁ ⁺	×	×	×	×	×	[51]	
37	2,4-Hexadienal/2-ethylfuran	97.064	C ₆ H ₉ O ⁺	×	×	×	×	×	[8]	
38	2-Hexenal (<i>E</i>)/2-methylcyclopentanone	99.080	C ₆ H ₁₁ O ⁺	×	×	×	×	×	[8]	
39	Ethyl 2-propenoate	101.059	C ₅ H ₉ O ₂ ⁺	×	×	×	×	×	[8]	
40	Hexanal	101.096	C ₆ H ₁₃ O ⁺	×	×	×	×	×	[44]	
41	1-Hexanol/butyl formate	103.075	C ₅ H ₁₁ O ₂ ⁺	×	×	×	×	×	[44]	
42	Xylene/ethylbenzene	107.085	C ₈ H ₁₁ ⁺	×	×	×	×	×	[26]	
43	Terpenes fragments	109.101	C ₈ H ₁₃ ⁺	×	×	×	×	×	[51]	
44	n.a.	115.078	C ₆ H ₁₁ O ₂ ⁺	×	×	×	×	×	n.a.	
45	Butyl acetate/propyl propanoate/(<i>E</i>)-2-hexen-1-ol	117.091	C ₆ H ₁₃ O ₂ ⁺	×	×	×	×	×	[44]	
46	Terpenes fragments	121.101	C ₉ H ₁₃ ⁺	×	×	×	×	×	[51]	
47	Phenethyl alcohol	123.116	C ₈ H ₁₁ O ⁺	×	×	×	×	×	[64]	
48	6-Methyl-3,5-heptadien-2-one	125.096	C ₈ H ₁₃ O ⁺	×	×	×	×	×	[13]	
49	Methyl hexanoate/heptanal	131.106	C ₇ H ₁₅ O ₂ ⁺	×	×	×	×	×	[44]	
50	<i>p</i> -cymene	135.116	C ₁₀ H ₁₅ ⁺	×	×	×	×	×	[26]	
51	Monoterpenes	137.132	C ₁₀ H ₁₇ ⁺	×	×	×	×	×	[8]	
52	Hexyl acetate/ethyl hexanoate/methyl heptanoate/butyl butanoate	145.122	C ₈ H ₁₇ O ₂ ⁺	×	×	×	×	×	[62]	
53	Sesquiterpenes fragments	149.132	C ₁₁ H ₁₇ ⁺	×	×	×	×	×	[52]	
54	Sesquiterpenes (copaene/farnesene)	205.195	C ₁₅ H ₂₅ ⁺	×	×	×	×	×	[44]	

The putative identifications was performed on the basis of exact masses provided by tool and compared with pears literature (or another fruits when not available), GC-MS data and fragmentation patterns (when available), and PTR-MS literature. Only signals with abundance higher than 1 ppbv were taken into account. The symbols indicate the presence (×) or absence (O) of compound

Fig. 1 Heat map of the protonated masses and one-dimensional dendrogram of the 120 spectral samples. VOCs are clustered by columns, samples are clustered by rows. W1, H1, Y1: William, Hosui, and Ya Li whole fruits, respectively; W2, H2, and Y2: William, Hosui, and Ya Li cube fruits, respectively. Cophenetic correlation coefficient: 0.8869

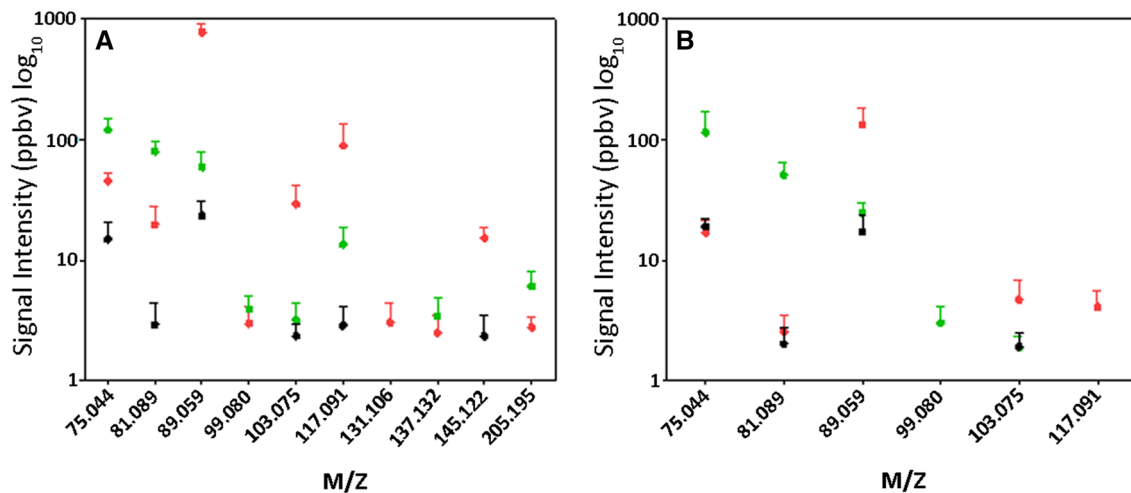
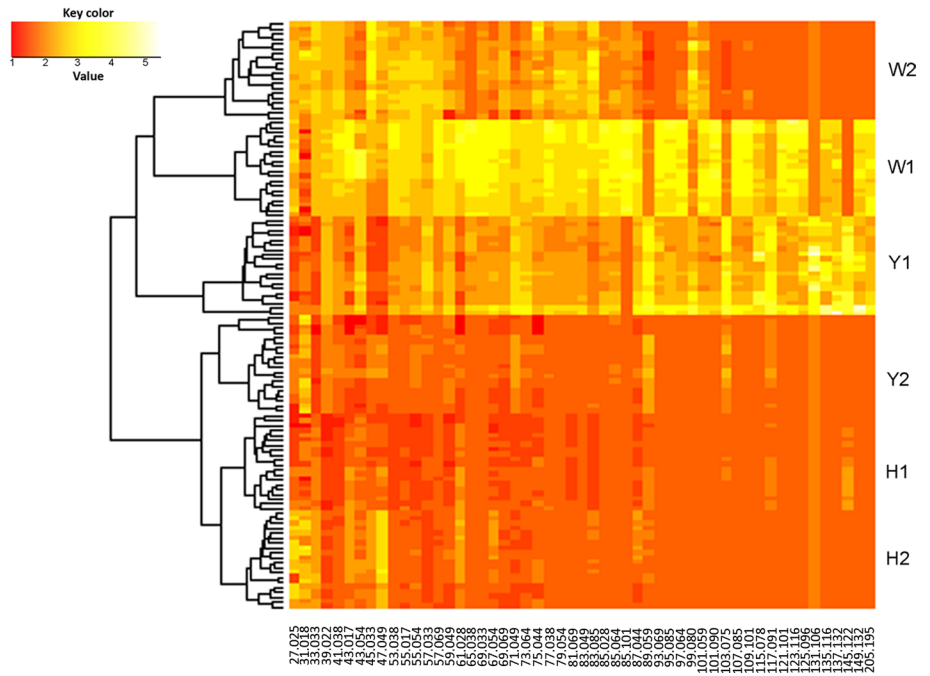


Fig. 2 Signal intensities of VOCs that possess strong pear-like aromas or are identified as impact volatiles in different varieties of pears such as: m/z 75.044 (TI: butanol), m/z 81.069, 89.059 (TI: ethyl acetate), m/z 99.080 (TI: 2-hexenal), m/z 103.075 (TI: 1-hexanol), m/z 117.091 (TI: butyl acetate/propyl propanoate), m/z 131.106 (TI: pentyl acetate), m/z 145.122 (TI: hexyl acetate/ethyl hexanoate), m/z 81.069, 137.132,

205.195 (TI: terpenes compounds) (Rapparini and Predieri [8]; Li et al. 2012). Figure **a** indicate the value detected from whole fruits sample, while **b** from the cube pear samples. Red point indicate *P. bretschneideri* (Ya Li), Green point *P. communis* (William) and the Black point *P. pyrifolia* (Hosui)

different pear samples (whole and cube samples), only the m/z presenting VIP scores higher than 2 and their possible identification were reported in Table 4 (m/z detected in “Hosui” cube samples always showed VIP scores lower than 2, for this reason we reported m/z with the highest VIP scores). In whole pear samples, the chemical species with the highest significance for the discrimination of the species/cultivars were (1) for “Williams”: m/z 33.033 (Putative

identification, PI: methanol); m/z 47.049 (PI: ethanol); m/z 89.059 (PI: ethyl acetate); m/z 99.080 (PI: 2-hexenal); m/z 145.122 (PI: hexyl acetate/ethyl hexanoate); (2) for “Ya Li”: m/z 33.033 (PI: methanol); m/z 45.033 (PI: acetaldehyde); m/z 47.049 (PI: ethanol); m/z 61.028 (PI: acetic acid/propanal); m/z 89.059 (PI: ethyl acetate); m/z 99.080 (PI: 2-hexenal); m/z 131.106 (PI: methyl hexanoate/heptanal); m/z 145.122 (PI: hexyl acetate/ethyl hexanoate); (3)

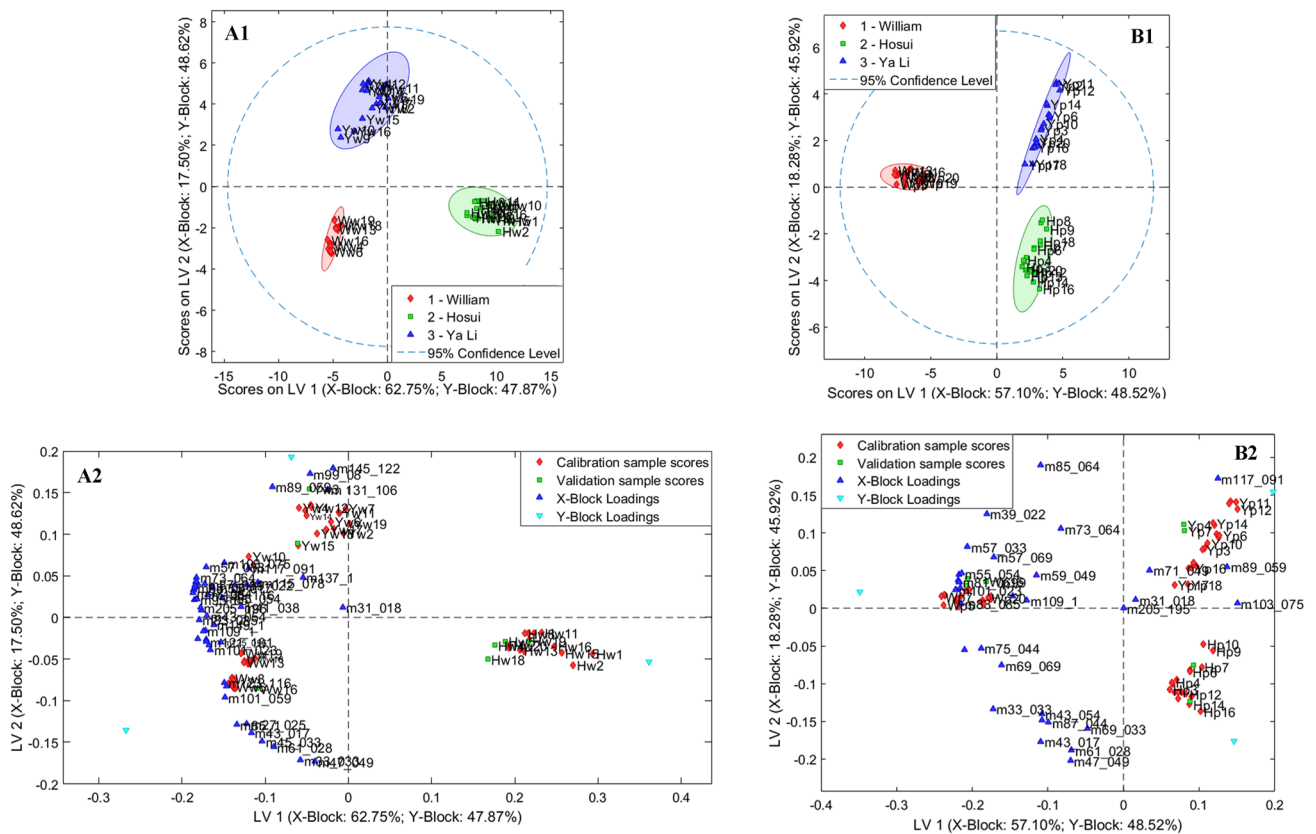


Fig. 3 **a** Scores (3A1) and Biplot (3A2) on LV1 and LV2 from PLS-DA of whole samples. **b** Scores (3B1) and Biplot (3B2) on LV1 and LV2 from PLS-DA of cubes samples

Table 3 PLS-DA statistics for whole fruits and cube samples, of three pear cultivars: whole samples: 1 = Hw, 2 = Ww, 3 = Yw; cube samples: 1 = Hp, 2 = Wp, 3 = Yp

Statistics	Whole fruits Y-BLOCKS			Cube samples Y-BLOCKS		
	Class 1 - Hw	Class 2 - Ww	Class 3 - Yw	Class 1 - Hp	Class 2 - Wp	Class 3 - Yp
Sensitivity (SE) (Cal)	1.000	1.000	1.000	1.000	1.000	1.000
Specificity (SP) (Cal)	1.000	1.000	1.000	1.000	1.000	1.000
Sensitivity (SE) (CV)	1.000	1.000	1.000	1.000	1.000	1.000
Specificity (SP) (CV)	1.000	1.000	1.000	1.000	1.000	1.000
Class. error (Cal)	0.000	0.000	0.000	0.000	0.000	0.000
Class. error (CV)	0.000	0.000	0.000	0.000	0.000	0.000
Class. error (Pred)	0.000	0.000	0.000	0.000	0.000	0.000
RMSEC	0.1056	0.0674	0.0890	0.0380	0.0879	0.0819
RMSECV	0.1137	0.0814	0.0983	0.0414	0.1007	0.0967
RMSEP	0.1280	0.0618	0.0947	0.0634	0.0837	0.0739

SE Sensitivity, SP specificity, RMSEC, RMSECV, RMSEP, Cal class. error for calibration, CV cross-validation, and Pred prediction, respectively

for “Hosui”: m/z 79.054 (PI: fragment of: xylene/ethylbenzene); m/z 83.085 (PI: C6 compounds/hexenol fragment); m/z 85.064; (PI: 1-penten-3-one) (Table 4). Conversely to

what expected, compounds emerged as good candidates for species selection in whole fruit samples of “Ya Li” were very similar to that of “Williams.” For example, masses

Table 4 Putative identification, mass-to-charge ratio (*m/z*), and VIP scores related to whole fruits and cube samples of the *Pyrus* species

Number of compounds	<i>m/z</i>	Putative Identification	VIP scores whole fruit "Williams"	VIP scores cube samples "Williams"	VIP scores whole fruits "Ya Li"	VIP scores cube samples "Ya Li"	VIP scores whole fruits "Hosui"	VIP scores cube samples "Hosui"
1	33.033	Methanol	2.41	1.48	4.70	2.50	0.49	2.75
2	45.033	Acetaldehyde	1.82	2.05	3.20	0.87	0.70	0.65
3	47.049	Ethanol	2.13	0.23	4.22	3.42	0.39	4.46
4	61.028	Acetic acid/propanol	1.92	0.20	3.55	2.85	0.62	3.51
5	79.054	Fragment xylene/ethylbenzene	0.73	2.28	0.16	0.86	1.37	0.47
6	83.085	C6 compounds/hexenol fragment	0.53	2.31	0.18	0.60	1.30	0.52
7	85.064	1-Penten-3-one	0.93	0.65	0.30	4.28	1.45	5.30
8	89.059	Ethyl acetate/ethyl ethanoate	2.25	1.31	4.07	2.22	0.56	1.68
9	99.080	2-Hexanal	2.38	2.37	4.74	0.85	0.41	0.49
10	117.091	Butyl acetate/propyl propanoate	0.50	0.84	0.48	4.07	0.54	2.75
11	131.106	Methyl hexanoate/heptanal	1.75	/	3.42	/	0.45	/
12	145.122	Hexyl acetate/ethyl hexanoate	2.59	/	5.22	/	0.20	/

Bold values correspond to protonated masses having VIP scores greater than 1 for the "Hosui" cube samples, greater than 2 for the others

of m/z 33.033 (PI: methanol) and m/z 45.033 (PI: acetaldehyde) (Table 4) were good indicators for both species. Moreover, “Ya Li” showed also m/z 47.049 (PI: ethanol) as valid candidate. These compounds are important precursors of natural fruits aroma and appear to be the result of anaerobic respiration during the normal ripening process [14].

Similarly, in cube sample pears, the model also allowed to correctly identify the taxonomic category of the three different *Pyrus* genotypes. Particularly, the compounds with highest VIP score for discrimination were (1) for “Williams”: m/z 45.033 (PI: acetaldehyde); m/z 79.054 (PI: fragment of: xylene/ethylbenzene); m/z 83.085 (PI: C6 compounds/hexenol fragment) and m/z 99.080 (PI: 2-hexenal); (2) for “Ya Li”: m/z 33.033 (PI: methanol); m/z 47.049 (PI: ethanol); m/z 61.028 (PI: acetic acid/propanal); m/z 85.064 (PI: 1-penten-3-one); m/z 117.091 (PI: butyl acetate/propyl propanoate); (3) for “Hosui”: m/z 33.033 (PI: methanol); m/z 47.049 (PI: ethanol); m/z 61.028 (PI: acetic acid/propanal); m/z 85.064 (PI: terpenes fragment); m/z 117.091 (PI: butyl acetate/propyl propanoate) (Table 4). Curiously, the ester compound detected at m/z 145.122 and putatively identified as hexyl acetate was found only in whole fruit samples within the group of Nashi pears, and not in “Williams” pears. On the other hand, methyl hexanoate (m/z 131.106) was detected only in “Ya Li” pears (Table 2; Fig. 2). The compounds mentioned above do not appear in “Hosui” whole samples, highlighting a very different profile compared to the other two pears.

Finally, in each cultivar, the discriminating compounds for cube sample pears were very different from those observed in the whole fruit. In this case, the good candidates for species discrimination were the same for the Nashi pears group, while they were deeply different from “Williams.”

Sensory measurements

The panel test results are summarized in Fig. 4; it was graphically reported the average scores of the eleven sensory attributes evaluated by the panelists. The judges agreement was tested by the calculation of the robust percentage of the variation coefficient. The CVr% of the descriptors always resulted below the established limit (≤ 20), demonstrating the reliability of the test. The sensory evaluation shown differences between the three species. In particular, “Hosui” cultivar recorded significant differences ($p = 0.01$) for crunchiness and firmness, showing the highest values with respect to the other two cultivars (Fig. 4). Interestingly, “Ya Li” pear emerged just for visual appearance parameter. On the other hand, the significant differences ($p = 0.01$) between “Williams” cultivar and both Nashi pears, were observed for graininess, sweetness, flavor, and aroma. The results of the panel test reflected those obtained by the physicochemical

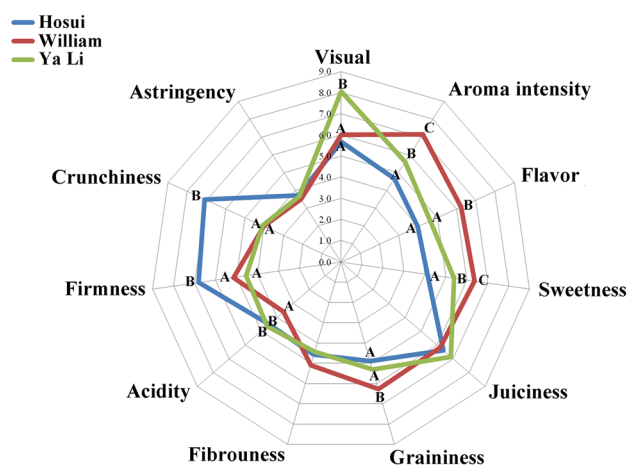


Fig. 4 Schematic representation of the average values of the scores of the 11 attributes of sensory analysis. Different capital letters indicate differences by the LSD test at the 99.0% confidence level ($p = 0.01$)

Table 5 Consumer acceptability: average scores (with standard deviation) and percentage of responses (level > 5 of the nine-point hedonic scale)

Species	Cultivar	Average scores	Responses percentage (%)
<i>Pyrus bretschneideri</i>	Hosui	5.18 ± 1.17 A	48
<i>Pyrus pyrifolia</i>	Ya Li	5.51 ± 0.80 A	55
<i>Pyrus communis</i>	Williams	7.43 ± 1.02 B	97

Different capital letter within a column indicates differences by the LSD test at the 99.0% confidence level ($p = 0.01$)

analyses. In fact, “Hosui” cultivar shown the highest firmness value, “Williams” the highest sweetness value, while the shape and the color of “Ya Li” obtained the highest score for visual appearance parameter.

The world pears market is characterized by similar quality requirements, even if different parameters can drive the customer preferences. The main attributes that drive consumer preferences are flavor and aroma, texture, shape, and visual appearance [60]. Among them, components like smell and aroma are the most interesting representing the basic components of eating pleasure [61]. Regarding the consumer test, significant differences ($p = 0.01$) were registered between Nashi and Williams pears. The average scores obtained by the Williams resulted higher (7.43 ± 1.02) than those shown by the two Nashi pears (5.18 ± 1.17 for Hosui and 5.51 ± 0.80 for Ya Li). Moreover, no significant differences ($p = 0.01$) were observed within Nashi pears (Table 5). The consumer acceptance was calculated as the percentage of respondents who liked the sample, with scores >5 and it has been observed that, the

97% of consumers expressed a positive opinion for “Williams”, 55% for “Ya Li” and 48% for “Hosui”. Thus, in the consumer opinion, the preferred pear was the Williams.

By pooling the VOCs and the panel test results, it was possible to perform a canonical correspondence analysis, which allows identifying those few aromatic molecules able to drive the consumers liking. In the triplot from CCOA, as a consequence of the combined effect of the selected VOCs (VIP) and the scores of two attributes of the sensory evaluation (aroma and flavor), cultivar “Williams” was clearly split from the Asian cultivars in the right part of the diagram and strongly linked to the aroma and flavor intensity (Fig. 5). In addition, the COOA highlighted a difference between the two Asian pears. The aroma and flavor arrows showed a similar trend and the “response” of each mass to the aroma and flavor projected onto each arrow was sequenced (Fig. 5). In particular, m/z 99.080 (PI: 2-hexenol) and 79.054 (PI: fragment of: xylene/ethylbenzene) were the most associated with both sensory attributes and contemporaneously with “Williams” cultivar, followed by m/z 85.064 (PI: 1-penten-3-one), linked to olfactory notes, and found,

even if in lower amount, also in “Ya Li” cultivar. The m/z 89.059 (PI: ethyl acetate) was negatively associated with the sensory variables: its amount was decreasing from “Ya Li” through “Hosui” to “Williams.” The m/z 83.085 (PI: C6 compounds/hexenol fragment) is responsible of aroma and flavor and it is typical of “Williams.” The m/z 117.091 (PI: butyl acetate/propyl propanoate), on average correlated to the sensory attributes, was only present in “Ya Li” samples. Finally, the position of the compounds 33.033 (PI: methanol), 45.033 (PI: acetaldehyde), 47.049 (PI: ethanol), and 61.028 (PI: acetic acid), clustered on the axes intersection, reflected approximately their amount in the different cultivars; these masses are ripening indicators and show a low correlation with the sensory attributes (aroma and flavor).

Conclusions

In this first study on pears, species originating from different geographical areas have been observed (1) important differences for VOCs and physicochemical parameters between Williams and Nashi pears, and also within Nashi pears; (2) relationships among sensory evaluation, physicochemical traits, and volatile compound profiles.

By pooling the entire dataset of physicochemical analyses, it emerged that the most of parameters (e.g., shape, skin color, sugar content) allow to distinguish the three species. The same behavior emerged by applying appropriate statistical data approach on VOCs fingerprinting; indeed, it was possible to perfectly discriminate each pear species. Moreover, using the VOCs analyses, differences between whole and cube fruits were shown, probably due to the skin presence. The differences (aroma and physicochemical parameters) highlighted among the pears, seemed to reflect the liking expressed by the panelists. Indeed, specific detected VOCs were also typical of some cultivars, so they could be used for cultivar discrimination purposes and to drive the consumer’s preferences. Furthermore, the consumer preferences could be also influenced by the higher sugar content and pear aroma (perceived by consumers) emitted by “Williams” cultivar. On the other hand, Nashi pears have been appreciated by the sensory evaluation (Panel test) for some characteristics such as firmness for “Hosui” and visual appearance for “Ya Li.” On the contrary, the lower sugar level and flavor intensity could have negatively influenced the consumer liking. Finally, consumers expressed a more positive opinion for “Williams” than for “Ya Li” and “Hosui.” Further exhaustive studies within and between different *Pyrus* cultivars may reveal new relationships between sensorial attributes and physicochemical traits and contribute to better design specific consumer profiles.

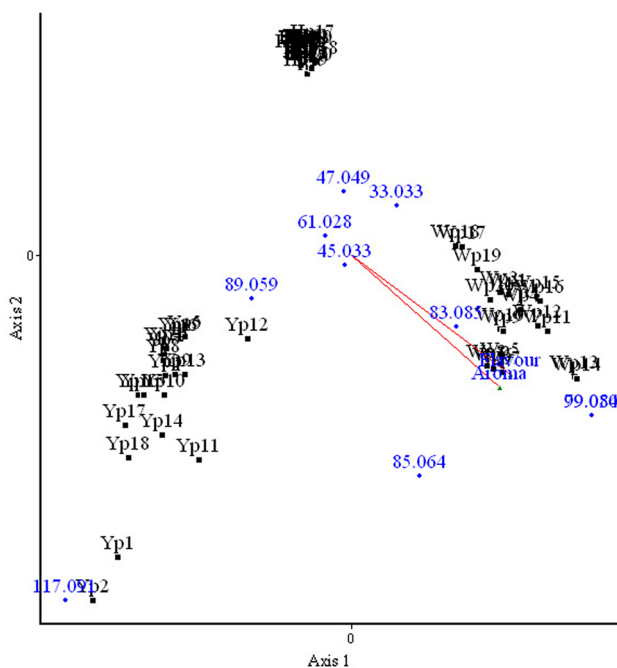


Fig. 5 Triplot from CCOA. The group (Wp, Hp, Yp) in which a given VOC has high proportions will be close to the position of that m/z . The sensory analysis (aroma and flavor) variables are also displayed, represented by arrows. The VOCs can be projected onto each arrow to derive a VOCs sequence with reflects approximately the response of the VOCs to that chemical-physical variable. In this way, VOCs positively or negatively correlated with the sensory variable can be identified. The length of arrows is proportional to the correlation of the variable with the axes

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Compliance with ethical standards

Conflict of interest We confirm that we do not have any conflict of interest.

Human/animal rights This article does not contain any studies with human or animal subjects.

Informed consent This article does not requires any informed consent.

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