**Aroma profile of a red plum purée processed by high hydrostatic pressure
and analysed by SPME–GC/MS**

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Abstract

The volatile profile of a plum purée (cv. *Crimson Globe*) processed by high hydrostatic pressure was evaluated by the method of solid-phase micro-extraction gas chromatography/mass spectrometry (SPME–GC/MS). Two pressure intensity levels and three holding times were applied (400 and 600 MPa for 1, 150 and 300 seconds) in order to know the effect of processing on the original aroma of plum purée. High pressure processed purées were compared to raw purée (unprocessed purée). A total of 40 volatile compounds were identified in the headspace of the plum purée. The major compounds identified were an aldehyde (hexanal) and two alcohols (hexan-1-ol and (Z)-hex-3-en-1-ol). The first two compounds were not affected by processing while the levels of (Z)-hex-3-en-1-ol were reduced at the less intense pressure treatments. Among the total volatile compounds isolated (40), 17 were not modified by high pressure processing (HPP) since no significant differences were observed after processing. The rest of the compounds (23) were significantly influenced by HPP. The modifications of these 23 volatiles represented changes of the 1.8% of the total aroma of the original purée. Significant differences were noticed in several compounds after the applied treatments, although the overall effect on the profile would not be significant. Results showed that the most intense treatments did not significantly alter the original aroma of plum purée. Therefore, HPP appears to be an alternative technology for the preservation of aromatic compounds of plum purée.

1. Introduction

Aroma profile of different food matrices has been extensively studied by means of the technique of gas chromatography coupled to mass spectrometry (GC/MS) in combination with different extraction techniques. An example of the extraction technique used is the headspace solid-phase microextraction (SPME). SPME technique is commonly used for the extraction of volatiles compounds in fruits (Balasubramanian & Panigrahi, 2011; Chai et al., 2012). SPME is a very useful technique for isolating volatiles compounds from liquid matrices in short time and in a simple way. The main advantages of this technique are detection limits, low cost, simplicity in handling and small amount of sample is required.

The volatile compounds present in fruits are formed by a complex mixture of different chemical groups of compounds that directly affect the sensorial quality of fresh and processed fruits. Many factors affect volatile profile including cultivar, ripening stage, environmental conditions, postharvest handling, the fruit sample, analytical methods and processing used (Muna Ahmed, Feng-Jie, Fei-Fei, Chun-Hua, & Jun, 2013). For example, volatiles compounds can contribute to monitoring the processing in Padrón-type peppers (Oruña-Concha et al., 1998).

As a consequence of thermal pasteurization, a decrease of freshness and sensory quality of fruits is inevitable, appearing a perceptible “cooked” smell and taste (Cerdán-Calero, Izquierdo, & Sentandreu, 2013). A way to avoid this loss of freshness is the use of non-thermal processes such as high hydrostatic pressure (Katsaros, Tsevdou, Panagiotou, & Taoukis, 2010). High pressure processing (HPP) is already used commercially for a great variety of fruit and vegetables products. Jams, juices, coulis, fruit blends and sauces are some of the products currently available on the markets (Barrett & Lloyd, 2012; Norton & Sun, 2008). In general, HPP has been shown to maintain the original flavour and taste of many food products with minimal changes due to the low processing temperatures (Dede, Alpas, & Bayindirli, 2007). In this way, the aroma profile of fresh fruits is not altered when they are processed by HPP, since the effect on the covalent bonds of low molecular-mass compounds such as volatiles compounds is very limited (Oey, Lille, Van Loey, & Hendrickx, 2008). In order to know how to maintain the original aroma of processed purées, several papers have evaluated the effect of HPP on the flavour compounds of fruits and vegetables products, such as tomato juice (Porreta, Birzi, Ghizzoni, & Vicini, 1995), strawberry coulis (Lambert, Demazeau, Largeteau, & Bouvier, 1999), cherry tomato purée (Viljanen, Lille, Heiniö, & Buchert, 2011), orange juice

(Baxter, Easton, Schneebeil, & Whitfield, 2005; Vervoort et al., 2012) or fruit smoothies (Keenan, Brunton, Mitchell, Gormley, & Butler, 2012).

Plum (*Prunus salicina* Lindl.) is one of the most economically important crops in Extremadura region, Spain (Lozano et al., 2009). The aroma of plums provides a reliable indicator of its quality and contributes to their final acceptance by the consumers (Chai et al., 2012). For that reason, some recent studies have evaluated the volatile aroma compounds of plums (Chai et al., 2012; Liu et al., 2009; Lozano et al., 2009; Louw & Theron, 2012; Pan & Yang, 2005; Pino & Quijano, 2012). Analysis of the volatile composition of plums includes esters, aldehydes, alcohols terpenes, acids, alkanes, ketones, lactones and phenols (Gómez-Plaza & Ledbetter, 2010; Nunes, Coimbra, Saraiva, & Rocha, 2008). In general, esters, aldehydes and alcohols are considered the most important classes of compounds involved in the perception of aroma in plums (Chai et al., 2012; Gómez-Plaza & Ledbetter, 2010). Although plums are mainly consumed as fresh fruit, surpluses or appropriate cultivars for industrial processing can be processed into purées which are the basis of a wide variety of products such as juices, nectars and jellies. In this sense, purées from red plum varieties have a great potential for increasing production and uses in many food formulations. Moreover, red plums are rich in nutritional compounds such as anthocyanins and phenolic compounds (Lozano et al., 2009). Nutritional compounds and original red colour of plum could be preserved after HPP (González-Cebrino et al., 2013). Limited research has been conducted to evaluate the effect of processing on the aroma profile of plums (Ismail, Williams, & Tucknott, 1981; Sabarez, Price, & Korth, 2000; Nunes, Coimbra, Saraiva, & Rocha, 2008). Moreover, no information has been reported about the effect of HPP on the aroma of plum. As far as we know, this is the first study about the changes of the volatile profile of plum after HPP. HPP could be an appropriate and efficient technique to preserve the typical aroma as alternative to traditional pasteurisation. As this regard, the results obtained could provide significant information about the global effect of pressure level and holding time on volatiles compounds of this fruit since changes in the aroma are caused by different degradation reactions. Therefore, the aim of this study was to evaluate the effect of the application of different pressure intensities and holding times of HPP on the volatile profile of a red plum purée (*Prunus salicina* Lindl. cv. *Crimson Globe*).

2. Material and methods

2.1. Plum samples and purée manufacture

The plum cultivar used in this study was Japanese type (*Prunus salicina* Lindl.) cv. *Crimson Globe*, which has both red peel and flesh. Plums at commercial ripening stage (based on colour and firmness) were obtained from Tanynature S.L. (Zurbarán, Badajoz, Spain). All fruit were stored in a controlled cold chamber at 4 °C and 90% of relative humidity before the manufacture of the purée (less than one week). Plums were washed in cold water, manually stoned, cut into small pieces and finely homogenized using an electric blender (Thermomix; Vorwerk, Madrid, Spain) for 1 min at maximum velocity. All purée were immediately mixed to avoid initial differences in the samples. Purée lots (200 g each) were vacuum-heat-sealed (ILPRA, UM 18-GAS DIG., Barcelona, Spain) in polyethylene plastic (9.3 mL O₂/m²/24 h at 0 °C) bags. Then, the packaged samples of purée were stored at -80 °C until HPP.

2.2. High pressure processing

HPP was applied in a semi-industrial discontinuous hydrostatic unit (Hiperbaric Wave 6000/55, Hiperbaric, S.A., Burgos, Spain), which used water as the pressure-transmitting medium. Purée samples (bags) were pressurized at six different processing combinations of pressure level and processing time (400 and 600 MPa for 1, 150 and 300 s). Come-up-times to target pressures of 400 and 600 MPa were 174 and 230 s, respectively. When the treatment finished, the decompression (come-down-time) took about 1 s. The initial temperature of the water in the high pressure vessel was set at 10 °C. When high pressure treatments at 400 and 600 MPa were applied, the temperature reached 20 °C and 25 °C, respectively due to the adiabatic compression, which was calculated as 2.5 °C per 100 MPa (Balasubramaniam, Ting, Stewart, & Robbins, 2004), since the temperature inside the vessel could not be measured due to there is no temperature monitoring system coupled to the pressure unit. After processing, the samples were immediately stored at -80 °C until the volatile analyses were carried out. Unprocessed plum purée (raw purée) was used as reference sample. All processing treatments were applied in triplicate. A total of 30 samples (bags) were analysed, 27 samples of high pressure processed purée and 3 samples of unprocessed purée.

2.3. Solid Phase Microextraction–Gas Chromatography/Mass Spectrometry analysis of volatile compounds

Headspace solid phase microextraction (HS–SPME) was the technique used for the extraction and concentration of volatiles compounds. In order to optimize the extractive procedure, preliminary extraction assays were carried out for distinct fibre exposure times and temperatures according to the literature consulted (Chai et al., 2012; Keenan et al. 2012; Riu-Aumatell, Castellari, López-Tamames, Galassi, & Buxaderas, 2004; Riu-Aumatell, López-Tamames, & Buxaderas, 2005). Fifteen grams of purée were placed in a 50 ml vial containing a magnetic stirrer and then 3 g of NaCl were added to facilitate the release of volatiles compounds. Samples were equilibrated at 40 °C for 5 min in a thermostatically controlled water bath followed by exposure of a SPME fibre coated with a 50/30 µm film thickness of Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) obtained from Supelco (Sigma-Aldrich, Bellefonte, PA, USA) into the vial and exposing it to the headspace of each vial for 40 min. The fibre was selected as it is highly sensitive for analysing a wide range of volatiles compounds (Riu-Aumatell et al., 2005; Kebede et al., 2013). Prior to use, fibre was preconditioned in the gas chromatography injection port at 270 °C for 60 min following the manufacturer's instructions.

The volatile compounds were desorbed into a Varian CP-3800 GC gas chromatograph coupled to a Varian Saturn 2200 MS (Varian Inc., Palo Alto, CA, USA). The SPME fibre was injected directly into the injection port set at 250 °C. Volatile compounds were separated using a capillary column (HP-5; 50 m x 0.32 mm x 1.05 µm; Agilent, Santa Clara, CA, USA). The carrier gas was helium at a constant flow of 1 ml/min. The oven temperature was set from 35 °C for 5 min, increasing 2 °C/min to 175 °C, and then increasing 25 °C/min to 300 °C, by optimizing the method used in previous studies (Lozano et al., 2009). The GC–MS transfer line was heated at 280 °C. The mass detector operated in electronic impact (EI) mode of 70 eV and source temperature of 230 °C with a speed of 0.7 scan s⁻¹ over a mass range of m/z 30–400 AMU in a 1 s cycle in a full scan mode. The volatiles compounds were identified by comparing their mass spectra to that of the NIST and Varian libraries. In addition, when it was possible, a confirmation was performed by matching the retention time and mass spectrum of commercially acquired standard solutions (Sigma–Aldrich, St. Louis, MO, USA).

2.4. Statistical analysis

The differences in the volatile compounds were analysed using the one-way analysis of variance (ANOVA). HSD Tukey's test ($p < 0.05$) was applied to compare the mean values of the volatile compounds at the different high pressure treatments. All these statistical treatments were performed using the SPSS program, version 17.0 (SPSS Inc., Chicago, IL, USA). The relationships between volatiles compounds and treatments were assessed by a principal component analysis (PCA). Mean values and standard error of the mean (SEM) are reported.

3. Results and discussion

Table 1 shows the relative abundance expressed as arbitrary area units ($\text{AAU} \times 10^4$) of the compounds detected in the volatile fraction of plum purée (unprocessed and high pressure processed purées), ordered by chemical families. A total of 40 volatile compounds were identified in the headspace of the plum purée. The identified compounds were 11 aldehydes, 6 alcohols, 11 esters, 4 terpenes, 3 aromatic compounds, 2 ketones and 3 compounds classified as others.

Analysis of the volatile composition of plum purée showed that aldehydes and alcohols were most represented classes of compounds in all chromatographic profiles for both unprocessed and processed samples, accounting for up to 85% of the total volatile fraction. Some authors have studied the aroma profile of other plum cultivars (Williams & Ismail, 1981; Nunes et al., 2008; Lozano et al., 2009; Chai et al., 2012; Louw & Therow, 2012; Pino & Quijano, 2012). In general, the profiles identified by these authors were different from those reported in our study. For instance, these studies reported a larger number of compounds (Chai et al., 2012; Pino & Quijano, 2012; Louw & Theron, 2012), more esters and less aldehydes (Chai et al., 2012) or even several lactones were identified in the aroma profile of plum (Chai et al., 2012; Louw & Therow, 2012). The differences observed may be due to several factors such as: a) the volatile isolation technique, b) the type of coating fibre used for the concentration of volatiles, c) the different cultivars studied, the climatic conditions and ripening stage of the cultivars, or d) the processing conditions.

The major compounds identified in the unprocessed plum purée were hexanal (39.9%), hexan-1-ol (32.3%), (Z)-hex-3-en-1-ol (9.6%), [(Z)-hex-3-enyl] acetate (5.0%), hexyl

acetate (4.3%), hex-2-enal (3.3%). In general, most of the volatiles isolated were present in very low concentrations (represented less than 1% of total AAU). The major compounds detected in the present study were also identified in plum by other authors (Gómez-Plaza & Ledbetter, 2010). The two most abundant compounds (hexanal and hexan-1-ol) were not modified after HPP. This fact would be of importance to preserve the original aroma of plum purées.

Among the total volatile compounds isolated (40), 17 were not modified by HPP since no significant differences were observed after processing. The rest of compounds (23) were significantly influenced by HPP. The contribution of these 23 volatiles to the total aromatic fraction represented between 18.8% (400 MPa/150 s) to 20.6% (unprocessed) of the total area of compounds. The modifications of these 23 volatiles only represented changes of the 1.8% of the total aroma of the original purée. However, individual threshold odour perception of each volatile compound would need to be taken into account in order to evaluate the impact of those compounds to the global aroma of plum. Among these 23 compounds, 19 showed significant differences between unprocessed purée and some of the HP treatments (table 1). Differences between unprocessed and certain processed purées would indicate that combinations of pressure and time could have an effect on the increase or decrease of some volatile compounds. HPP could indirectly alter the content of some volatile compounds by enhancing or retarding enzymatic and chemical reactions, which could lead to desirable and undesirable changes in overall aroma profile (Viljanen et al., 2011). The rest of compounds (pentanal, non-1-en-3-ol, [(E)-hex-2-enyl] acetate and ethyl decanoate showed differences only between specific HP treatments.

3.1 Aldehydes

In general, aldehydes can be related to green, grassy and herbaceous notes (Melgarejo et al., 2012). Usually, aldehyde class is likely to be the desirable volatiles, since they contribute to aromatic odours in plants (Apichartsrangkoon, Chaikham, & Srisajjalertwaja, 2014). Six of the eleven volatile aldehydes isolated were modified after HPP (Table 1). The total AAU of the aldehydes isolated was slightly increased after HPP, except in purées processed at the less intense conditions (400 MPa/1 s) which showed similar total amounts as unprocessed purées. The higher increase of aldehydes was found in purées processed at 400 MPa/300 s.

Hexanal was not affected by HPP, being the major aldehyde and representing more than the 75% of the total area of aldehydes. In addition, hexanal is a volatile compound associated with the smell of foliage and grass and has been described as having a plum-like aroma (Chai et al., 2012) so it might add pleasant flavour to plum purée.

Previous studies have found changes in the hexanal content of fruits and vegetables as a result of HPP. For instance HPP at 400 MPa for 20 min greatly increased the hexanal content of strawberry purée (Navarro, Verret, Pardon, & El Moueffak, 2002). On the contrary, pressurization at 800 MPa (also for 20 min) resulted in a slight decrease in the hexanal content (Lambert et al., 1999). Viljanen et al. (2011) observed that cherry tomato purée treated at 800 MPa for a holding time of 10 min (at ambient temperature) enhanced the levels of hexanal.

The increases in the levels of hexanal are considered as a result of the oxidation of free fatty acids, such as linoleic and linolenic acid. Lipoxygenase and hydroperoxide lyase are naturally present in many vegetables and fruits, and are partially responsible for the formation of lipid derived volatile odour compounds such as hexanal (Viljanen et al., 2011). Sumitani, Suekane, Nakatani, & Tatsuka (1994) attributed the increase of hexanal in peach pieces to the disruption of the fruits tissues when they were pressurized at 400 MPa. This phenomenon may not happen in plum purée as the relative amounts of hexanal were maintained after processing.

The maintenance of the levels of hexanal, and other minor aldehydes such as 2-methylbutanal, hexa-2,4-dienal, heptanal, and oct-2-enal could be positive for the preservation of the fresh like aroma of plum purée after processing.

On the other hand, other aldehydes, which were also isolated in this purée, were significantly modified after HPP. Hex-2-enal was the second most abundant aldehyde isolated in the headspace of the plum purée. Unprocessed purée had the lowest significant levels of this compound while the highest level was found in samples processed at 600 MPa/150 s. Hex-2-enal adds 'green grass' and also 'sweet and fruity' (apple, plum) notes (Fenaroli, 2002).

Other minor aldehydes such as acetaldehyde, pentanal, nonanal, decanal, and dodecanal were also modified after HPP. Acetaldehyde, pentanal and dodecanal were gradually increased at highest pressure intensities and holding times, so the highest levels of these compounds were detected at 600 MPa for 300 s. For example, when purée was pressurized at 600 MPa for 300 s, changes in the concentration of acetaldehyde was

observed compared to unprocessed and the rest of HP processed purées (Table 1). By contrast, the levels of nonanal decreased when purées were treated at 400 MPa/300 s and 600 MPa/1 and 150 s. Nonanal is a characteristic constituent of skin waxes of plums and its presence is associated with floral-fruit aroma, having a fragrant, woody-like aroma (Lambert et al., 1999; Ismail, Williams, & Tucknott, 1981; Williams & Ismail, 1981). Nonanal was also found to be a dominant aldehyde in most plum cultivars (Chai et al., 2012; Pino & Quijano, 2012). Pentanal showed differences between samples treated at 400 MPa/1 s and samples treated at 600 MPa for 150 and 300 s (Table 1).

3.2 Alcohols

Alcohols were the second chemical group of compounds more abundant in the plum purée. They represent the 42.3% of the total AAU of the compounds isolated in the unprocessed purée. Six alcohols were detected in plum purées (Table 1). Among the six alcohols isolated, three were modified by HPP (hex-3-en-1-ol, oct-1-en-3-ol and non-1-en-3-ol). In general, a little decrease in the total AAU of alcohols was observed after HPP.

Hexan-1-ol, which was the second most abundant contributor of the aroma of plum purée, was not modified after HPP, although a small decrease was observed in their levels after processing. A similar trend was found for the second most abundant alcohol detected in the present study, hexen-3-ol. In this case, a significant decrease in the level of this compound was found in the processed purées at less intense conditions (400 MPa at 1 and 150 s) respect to the unprocessed purée. Hexan-1-ol and hexen-3-ol are considered important contributors to the aroma of fresh plums (Pino & Quijano, 2012). Hexanol is formed in plant tissues by the activity of the enzyme alcohol oxidoreductase on hexanal (Wongfhun, Gordon, & Apichartsrangkoon, 2010). The levels of hexanol were similar as unprocessed purées which could indicate that HPP did not affect the oxidoreductase activity. A decrease of the levels of hex-3-en-1-ol might be related to the reaction and/or transformation of this compound into other reactants.

The levels of oct-1-en-3-ol and non-1-en-3-ol were significantly increased when samples were pressurized at the less intense processing conditions at 400 MPa for 1 s (both compounds) and 150 s (only oct-1-en-3-ol). Oct-1-en-3-ol has a powerful, sweet, earthy odour with herbaceous note reminiscent of hay and mushrooms (Fenaroli, 2002; Jordán et al., 2003).

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3.3 Esters

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Esters play an important role in the characteristic aroma of many fruits, contributing to fruity and floral notes (Chai et al., 2012; Yang, Balandrán-Quintana, Ruiz, Toledo, & Kays, 2009). Esters were also abundantly isolated in the headspace of different varieties of plum (Chai et al., 2012). In our study, numerous types of esters were isolated (11 compounds), although the levels were relatively low (about 11% of the total content of volatile compounds). Pino & Quijano (2012) found that esters were qualitatively and quantitatively the most abundant class of volatiles compounds of fresh plums, although the volatile compounds were isolated by means of simultaneous distillation-extraction (SDE) using diethyl ether, and differences could be explained by the different methods of extraction.

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The levels of most esters decreased during the high pressure treatments (Table 1), while only the levels of (Z)-hex-3-enyl acetate and hex-3-enyl benzoate were not modified after processing. Among the esters identified, (Z)-hex-3-enyl acetate was quantitatively the major ester isolated. It provides fruity and herbal odours (Yang et al., 2009), so the lack of changes after HPP in the levels of this compound would be positive to preserve the original aroma of purée. Pentyl acetate were also found in plums by other authors (Pino & Quijano, 2012; Chai et al., 2012).

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A decrease of the levels of esters such as ethyl acetate, hexyl acetate, hex-3-enyl hexanoate, hex-3-enyl butanoate, hexyl butanoate and pentyl acetate after HPP would decrease the pleasant flavour of fruit purée (Chai et al., 2012; Yang et al., 2009). Concretely, hexyl acetate, the most abundant of these esters, provides fruity and herbal notes (Yang et al., 2009). Ethyl acetate has a pleasant ethereal-fruity, brandy-like odour (Fenaroli, 2002). Hex-3-enyl hexanoate has been identified with a fruity-green and prune odour in guava purée (Jordán et al., 2003). Pentyl acetate and others esters possess strong pear-like aromas (Komes et al., 2007; Rapparini & Predieri, 2003). Hexyl butanoate has been described as fruity, apple and peel-like aroma (Bugaud & Alter, 2016).

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On the other hand, some esters such as hex-2-enyl acetate and ethyl decanoate decreased at the less intense treatment conditions but increased when the highest pressures and holding times (600 MPa / 300 s) were applied. So, in this case, the most intense HP treatments would be positive to preserve some pleasant aroma compounds. In the same line, Keenan, Brunton, Mitchell, Gormley, and Butler (2012) supported that

pressurization (600 MPa/20 °C/15 min) preserved some esters in fruit smoothies implied in fruity and fresh aroma.

3.4 Terpenes, aromatic compounds, ketones and other compounds

Volatile terpenes are important compounds for the flavour and fragrance of fruits since they are responsible for a wide range of pleasant aromas (Nunes et al., 2008; Jiang & Song, 2010; Chai et al., 2012). In this study, the total content of terpenes accounted for 0.3–0.5% of total volatiles (Table 1). Of the 4 terpenes isolated (β -cycocitral, β -ionone, β -damascenone and geranyl acetone), only β -ionone was affected by HPP. Purée processed at 400 MPa for 1 s contained the higher β -ionone content than unprocessed purée. β -ionone, β -damascenone and geranyl acetone were also identified by Pino & Quijano (2012) in plum cv. *Horvin*.

Among the three aromatic compounds detected in the plum purée, only benzaldehyde was significantly modified after HPP. Benzaldehyde is considered an important contributor to the aroma of fresh plums (Gómez-Plaza & Ledbetter, 2010). HPP at 400 MPa /1 s increased the levels of benzaldehyde, while purées processed at 600 MPa/1 s showed lower content respect to the unprocessed purée. Sumitani et al. (1994) also reported an increase of this compound after processing a peach purée at 400 MPa. They indicated that the increase in benzaldehyde content was probably caused by the remaining activity of the enzyme β -glucosidase. Benzaldehyde is formed from benzyl alcohol, by oxidation catalysed by dehydrogenases (Dudareva, Pichersky, & Gershenzon, 2004) and also by enzymatic degradation of the cyanogenic glycosides amygdalin and prunasin from *Prunus* spp. (Poulton, 1993).

The ketones content was low in the purées, accounting for less than 0.3% of the total volatiles (Table 1). Only two ketones were detected in this study, 6-methyl-5-hepten-2-one and nonan-2-one. Nonan-2-one content was affected by HPP while 6-methyl-5-hepten-2-one content remained unchanged. Processing at 400 MPa/1 s increased nonan-2-one content, while purées processed at 600 MPa for 1 and 150 s showed similar levels as unprocessed purée.

Other compounds detected were hexanoic acid, pentadecane, and furan 2-ethyl which contributed only 0.4–0.5% of total volatiles. HPP produced significant changes in the levels of hexanoic acid and furan 2-ethyl. Hexanoic acid levels were significantly increased in the

purées processed at 600 MPa for 300 s. In contrast, furan 2-ethyl decreased after some HPP conditions (400 MPa/1 s and 600MPa/150 s). This compound has been also isolated from plums of 'Japanese' cultivars ('Angeleno' 'Songold' and 'Laetitia') (Louw & Theron, 2012).

3.5 Principal components analysis

A principal component analysis (PCA) was carried out to determine which treatment would better preserve the original aroma of plum purée. Generally, two principal components are sufficient to explain a great proportion of the variation in the original variables, thus resulting in a considerable compression of the data. In this study, 37% and 19% of the variability was explained by principal components (PC) 1 and 2, respectively. Figure 1 shows the score plot of the different variables (coefficients of the eigenvectors) for the two first principal components (PC 1 and PC 2). Only most abundant volatile compounds of each chemical group were included in the analysis.

The distribution of the scores on the first two PCs (Figure 2) shows only 2 separate groups of points, corresponding to non-treated and treated purées. The distribution of the individuals could be explained only by the PC 2. On the positive axis of PC 2, far from the origin and explaining an important part of the variation are located volatile compounds associated to untreated purée, principally esters such as ethyl acetate, hex-3-en-1-ol, hexan-1-ol, hexyl, acetate. On the negative axis of PC 2 are located the compounds that were increased after HPP such as hex-2-enal or the benzaldehyde. However, this PC 2 explains only a relatively low percentage of the variance (19%). In addition, the PCA could not explain the differences due to the application of the different HPP conditions and a not clear pattern of changes of volatile compounds was found in the purées after processing. Only differences between non-treated and treated purées were found. In consequence, it is difficult to decide which treatment conditions (pressure and holding time) are more appropriate to preserve the original aroma of this product. Results of the PCA, globally explain results previously showed for each chemical group. Some differences were found between control and processed purées in compounds such as esters, but in general the volatile profile was well-preserved by HPP. In addition, the effect of the different treatments applied did not produce a clear effect on the changes of aroma.

The evaluation of the changes in the aroma profile could serve as indicator of the global variations that are produced after processing (Vervoort et al., 2012) which allows a

general evaluation of the effect of specific processing conditions. In a previous study (González-Cebrino, Durán, Delgado-Adámez, Contador, & Ramírez, 2013) we evaluated the effect of HPP on the physicochemical parameters, bioactive compounds, and polyphenol oxidase activity in a plum purée from the same fruit variety. We concluded that HPP did not affect adversely the nutritional quality of the plum purée, so that HPP seems to be an efficient method to preserve a plum purée with an acceptable nutritive value. Results of this paper would be in line with that study, since the modifications of the volatile profile were not marked and in general the original aroma was preserved after HPP.

4. Conclusions

HPP is an attractive technology for the preservation of the original aroma of plum. All purées (non-processed and high pressure processed) showed a similar volatile profile, although some significant differences were noticed in several compounds such as esters. Esters were the family of compounds most affected by HPP. The levels of most esters slightly decreased after the treatments. In addition, the pressure level and the holding time had a similar effect on the aroma profile of plum, so the effect on other parameters, such as the microorganisms/enzymes inactivation would be decisive to decide the most adequate processing conditions to reach an adequate shelf-life of the processed product.

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Table 1. Volatile compounds (area units $\times 10^4$) isolated in the plum purée after high pressure processing (HPP) at 400 and 600 MPa for 1, 150 and 300 s

Compounds	Id. Method ¹	Non-treated	400 MPa			600 MPa			SEM	p-value	Descriptors ²
			1 s	150 s	300 s	1 s	150 s	300 s			
Aldehydes											
Acetaldehyde	RF	18.3ab	11.6c	14.0bc	14.1bc	14.1bc	15.0abc	19.3a	0.7	0.003	pungent, ether
2-Methylbutanal	TI	16.1	11.4	13.6	15.3	13.8	15.8	14.6	0.5	0.095	cocoa, almond
Pentanal	RF	38.0abc	34.6c	37.7bc	39.2abc	37.4bc	41.7ab	43.1a	0.7	0.002	almond, malt, pungent
Hexanal	RF	8667.0	8462.5	9069.8	9245.5	9161.2	9175.5	8849.2	85.1	0.073	grass, tallow, fat
(2Z,4E)-Hexa-2,4-dienal	TI	106.7	115.0	105.7	116.5	100.5	105.9	115.9	2.4	0.474	green
Hex-2-enal	TI	721.9c	832.6ab	812.8ab	851.9ab	775.3bc	890.0a	862.6ab	13.3	0.001	apple, green, leaf
Heptanal	TI	17.0	18.5	18.3	18.0	16.9	17.8	17.2	0.2	0.110	fat, citrus, rancid
(E)-Oct-2-enal	TI	14.2	19.4	18.0	18.9	15.2	18.1	19.7	0.7	0.258	green, nut, fat
Nonanal	RF	99.1a	113.3a	100.2a	81.0b	74.1b	71.1b	108.9a	3.7	0.001	soap, orange peel, tallow
Decanal	RF	17.1ab	17.0ab	18.3a	16.4ab	13.8bc	12.6c	17.0ab	0.5	0.001	
Dodecanal	RF	11.1b	12.0b	12.5b	12.1b	15.8ab	18.7ab	24.5a	1.2	0.008	lily, fat, citrus
Subtotal		9726.5	9647.9	10220.9	10428.9	10238.1	10382.2	10092.0			
Alcohols											

Octan-1-ol	TI	15.2	15.4	15.9	16.3	15.1	14.5	13.6	0.5	0.821	chemical, metal, burnt
(Z)-Hex-3-en-1-ol	RF	2078.8a	1697.8b	1645.7b	1808.5ab	1886.8ab	1852.5ab	1937.5ab	37.3	0.010	green, grass
Hexan-1-ol	RF	7015.8	6426.7	6326.2	6562.0	6382.8	6463.3	6787.8	70.0	0.055	resin, flower, green
2-Ethylhexan-1-ol	TI	23.5	29.7	27.7	26.5	25.3	24.1	24.4	0.8	0.402	rose, green
Oct-1-en-3-ol	TI	11.3b	14.8a	14.9a	13.1ab	12.0ab	13.6ab	14.1ab	0.4	0.018	mushroom
Non-1-en-3-ol	TI	32.6ab	42.6a	24.1b	35.8ab	30.7ab	30.0ab	37.2ab	1.7	0.049	intensely oily creamy green earthy mushroom
<i>Subtotal</i>		9177.2	8227.0	8054.5	8462.2	8352.7	8398.0	8814.6			
Esters											
Ethyl acetate	RF	84.0a	47.7c	54.8c	57.7c	57.4c	60.0bc	71.5b	2.7	0.001	pineapple
Hexyl acetate	RF	930.0a	840.0ab	782.4ab	774.2ab	727.3b	721.8b	773.7ab	18.4	0.010	fruit, herb
[(Z)-Hex-3-enyl] acetate	TI	1075.7	1060.5	984.8	1000.3	948.4	947.6	1052.7	15.9	0.110	green, banana
[(E)-Hex-2-enyl] acetate	TI	71.8ab	58.2b	63.8b	64.6b	72.1ab	61.3b	94.5a	3.1	0.011	sweet leafy green with a fresh, fruity, apple nuance
Pentyl acetate	TI	44.8a	23.6b	23.2b	21.7b	17.8b	20.8b	30.6ab	2.3	0.004	ethereal fruity banana pear banana apple
[(Z)-Hex-3-enyl] butanoate	TI	37.4a	31.6ab	26.5b	25.6b	23.6b	22.3b	27.8ab	1.3	0.006	wine, green
Hexyl butanoate	TI	45.7a	39.1ab	33.7ab	31.1b	30.6b	30.7b	38.6ab	1.5	0.016	apple peel

[(Z)-Hex-3-enyl] hexanoate	TI	16.0a	13.0ab	11.8ab	10.5b	10.5b	9.0b	12.7ab	0.6	0.009	fruit, prune
Hexyl hexanoate	TI	13.8b	20.3a	18.5ab	17.8ab	15.7ab	15.3ab	14.6ab	0.6	0.022	
											apple peel, peach
[(E)-Hex-3-enyl] benzoate	TI	101.8	139.5	124.9	120.2	111.0	114.0	126.4	4.0	0.236	green, sweet, oily, floral, spicy, with fruity undertones
Ethyl decanoate	RF	45.0ab	41.4ab	48.6ab	35.9b	34.8b	39.2ab	58.1a	2.1	0.019	grape
<i>Subtotal</i>		2466.0	2314.9	2173.0	2159.6	2049.2	2042.0	2301.2			
Terpenes											
β-Cyclocitral	TI	23.0	27.7	22.3	25.4	20.4	22.2	25.0	0.8	0.165	mint
β-ionone	TI	21.5b	40.0a	35.3ab	32.9ab	32.9ab	30.9ab	32.2ab	1.6	0.050	seaweed, violet, flower, raspberry
<i>trans</i> - Geranylacetone	TI	13.0	13.9	12.9	11.4	9.1	10.6	10.9	0.6	0.385	magnolia, green
β-Damascenone	TI	14.3	15.0	16.8	19.3	15.4	16.4	17.0	1.0	0.935	apple, rose, honey
<i>Subtotal</i>		71.8	96.6	87.2	91.7	77.8	80.2	85.1			
Aromatic compounds											
Benzaldehyde	RF	62.2b	79.3a	68.7ab	74.2ab	63.3b	67.3ab	69.6ab	1.6	0.014	almond, burnt, sugar

Benzyl alcohol	TI	63.1	74.0	67.2	64.4	61.0	61.9	57.7	2.2	0.590	sweet, flower
Toluene	RF	11.5	8.3	7.5	12.9	8.0	8.2	12.2	0.7	0.128	paint, sweet
<i>Subtotal</i>		136.8	161.6	143.4	151.5	132.3	137.4	139.5			
Ketones											
5-Hepten-2-one. 6-methyl-	TI	38.0	41.3	39.7	35.8	31.5	35.2	37.6	1.1	0.280	fruity, apple, musty, ketonic and creamy with slight cheesy and banana nuances
Nonan-2-one	RF	12.8b	18.4a	16.1ab	15.1ab	13.7b	13.9b	14.7ab	0.5	0.017	hot milk, soap, green
<i>Subtotal</i>		50.8	59.7	55.8	50.9	45.2	49.1	52.3			
Other compounds											
Hexanoic acid (Caproic acid)	TI	48.0b	64.7ab	46.2b	49.8b	46.3b	47.9b	77.6a	2.8	0.001	sweat
n-Pentadecane	RF	18.4	23.5	20.0	17.9	17.7	18.6	18.8	0.7	0.410	wax
Furan 2-ethyl-	TI	11.0a	7.8b	8.3ab	8.8ab	9.0ab	7.5b	8.6ab	0.3	0.016	chemical-like with a beany bready malty nuance
<i>Subtotal</i>		77.4	96.0	74.5	76.5	73.0	74.0	105.0			
Total		21706.5	20603.7	20809.3	21421.3	20968.3	21162.9	21589.7			

554 ¹ Method of identification: RF, mass spectrum and retention time identical with a reference compound; TI, tentative identification by mass spectrum. SEM: Standard
555 Error of the Mean. a, b, c: different letters in the same row indicate significant statistical differences (Tukey's Test, $p < 0.05$).

556 ² Flavor descriptors from the Cornell University FlavorNet (<http://flavor.net/html>) and the Good Scents Company
557 (<http://www.thegoodscentscompany.com/index.html>).

Figure 1. Loading plots after principal components analysis of the variables in the plane defined by the two first principal components (PC 1 and PC 2).

Figure 2. Scores plot after principal component analysis of the individuals in the plane defined by the two first principal components (PC 1 and PC 2).