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Study of the volatile components of a candied plum and estimation of their contribution to the aroma

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ABSTRACT

A methodology comprising the combination of sample analysis by simultaneous distillation and extraction (SDE) and headspace analysis by solid phase microextraction (HS-SPME) is proposed to characterise the volatile fraction and to estimate its contribution to the aroma properties of heat treated sugar-rich fruits. In the present study, the volatile composition of "Ameixa d'Elvas", a traditional candied plum, was established by SDE. It reflects the complexity of the reactions and rearrangements that happen during the fruit ripening plus those occurring due to the thermal processing in presence of sucrose. HS-SPME allowed to detect the volatile compounds present in the headspace of the intact pulp, potentially responsible for the aroma properties. Eleven compounds were determined as the would-be impact odourants of "Ameixa d'Elvas", which are associated with sweet, cooked, and fruity odours. All would-be impact odourants of "Ameixa d'Elvas" fruits, except one, were also detected in the sucrose syrup headspace where the fruits have been submersed. This study indicates that, together with the pulp of the processed fruit, syrup contains compounds that can contribute to the aroma of candied fruits.

1. Introduction

"Ameixa d'Elvas" is a "Protected Designation of Origin" recognised by the European Union for a processed plum from Elvas (south–east of Portugal) obtained by a traditional candying process. Only the fruits of a special type of Green Gage plum, 'Rainha Cláudia Verde' (*Prunus domestica* L.) variety, can be utilised to produce "Ameixa d'Elvas". The candying process consists of boiling the intact plums in water for 15 min and then putting them in sucrose syrup, which is successively concentrated until 75 °Brix. The plums can be consumed with this syrup or, alternatively, can be stored in the syrup until being washed and packed in a solid state. Several chemical reactions occur during "Ameixa d'Elvas" processing, the composition of which has not been described objectively before (Diário da República, 1994), nor identified.

Analysis of the volatile composition of fresh plums showed that the esters are qualitatively the most important class of compounds (Crouzet, Etievant, & Bayonove, 1990). Quantitatively, they are also the major components of the volatile composition of fresh plums, followed by alcohols or aldehydes, depending on the cultivar and on the methodology used for volatile extraction. The contribution of these components for the overall aroma has been evaluated calculating their sensory perception limit (SPL) values in model matrices. Nonanal, 1-hexanol, *cis*-3-hexenol, linalool, benzaldehyde, γ-octalactone, and γ-decalactone were considered as important contributors to the aroma of fresh plums (Crouzet et al., 1990; Williams & Ismail, 1981).

The aroma of fruits can change on heating due to the liberation of volatile compounds from glycosidic precursors, oxidation, water addition, and cyclisation of individual compounds, such as hydroxy acids (Belitz, Grosch, & Schieberle, 2004). Thermal processes applied to plums induce modifications of their volatile composition, which have been described in the literature for several types of thermal processes in the presence of high quantities of sucrose (Crouzet et al., 1990; Ismail, Williams, & Tucknott, 1980b). The thermal processing is known to induce chemical modifications of the product components, mainly sugars and amino acids, leading to the production of a wide spectrum of flavour compounds. Carbonyl compounds are important for the aroma in heated processed plums, being benzaldehyde, furfural, 2-furfurylmethylketone, and nonanal the major constituents of the headspace and giving rise to almond-like and woody sensory descriptors (Ismail et al., 1980b). The molecules present in the headspace are indeed responsible for the smell that is perceived by the olfactory system if they are in concentrations above their SPL.

An approach to estimate the contribution of the volatile compounds to the aroma is the calculation of the aroma index (*I*) for each compound and the identification of the would-be impact odourants (Rocha, Rodrigues, Coutinho, Delgadillo, & Coimbra,

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2004). This was done relating the estimated concentration of each volatile component by simultaneous distillation and extraction (SDE), followed by gas chromatography–quadrupole mass spectrometry (GC–qMS) analysis, with the corresponding SPL value reported in the literature. This methodology, which does not include the use of sensory panel and/or GC–olfactometry studies, has been shown to be suitable as a preliminary step for estimating the potential contribution of the volatile components to the aroma properties. However, rearrangements, hydrolysis or artefact compound generation during water distillation, due to decomposition of the matrix components and impurities that may be introduced from solvents, have been extensively reported (Boulanger & Crouzet, 2000; Chaintreau, 2001; Kataoka, Lord, & Pawliszyn, 2000). As SDE promotes an exhaustive extraction and provokes the dispersion of the solid sample in the liquid phase, it is possible that not all the compounds recovered by SDE are emitted by the intact sample and/or occur in their headspace.

Solid phase microextraction (SPME) is a rapid, easy, solvent-free and sensitive sampling technique, evidenced by studies from a large number of fruits and products (Kataoka et al., 2000). The methodology that comprises SPME associated with GC–qMS is able to identify and quantify the volatile compounds, namely the compounds that occur in the headspace of different matrices. An advantage of SPME over the conventional solvent extraction methods is that the extracts do not have to be concentrated prior to analysis, preventing losses of low boiling point volatiles, such as short chain acids, alcohols and aldehydes (Chaintreau, 2001; Rocha, Ramalheira, Barros, Delgadillo, & Coimbra, 2001), and could allow their detection, which is usually impossible to do due to their co-elution with the solvent. Using SPME it is also possible to analyse the volatile composition present in the headspace of fruits, which is potentially responsible for their aromas. SPME technique also allows evaluating the formation of compounds during SDE due to oxidation and/or thermal reactions.

The aim of this work is to study the volatile composition of a traditional product, "Ameixa d'Elvas" plums, and estimate the contribution of the volatile compounds to the aroma, identifying the would-be impact odourants present in the plum's headspace. The volatile composition was determined using SDE followed by GC–qMS analysis and calculating the aroma index for each compound. HS-SPME coupled to GC–qMS was used to evaluate which of the volatile compounds identified as having $I > 1$ were in fact present in the headspace of "Ameixa d'Elvas" (would-be impact odourants). Furthermore, the headspace volatile profile of the 75 °Brix sucrose syrup used to process and store "Ameixa d'Elvas" was also studied by HS-SPME–GC–qMS.

2. Materials and methods

2.1. Samples

Plums of "Rainha Cláudia Verde" (*Prunus domestica* L.) variety in a precisely established stage of ripening (16–17 °Brix, pH 3.3, and titratable acidity of 1 meq of malic acid per 100 g of plum) were boiled in water for 15 min. The intact boiled plums were then immersed in 60 °Brix sucrose syrup. The solution was concentrated to 65 °Brix in the following day and to 75 °Brix after 7 days. The plums were stored, in storage tanks containing 400 kg of fruits, two months in the 75 °Brix sucrose syrup, the concentration of which was occasionally (2 or 3 times) corrected due to its hygroscopicity. The processed plums (10 kg), "Ameixa d'Elvas", were collected in the factory, Confibor Lda, Estremoz, Portugal, brought to the laboratory and maintained in their 75 °Brix syrup until analyses.

2.2. Materials

Dichloromethane used was of analytical grade and was purchased from Sigma-Aldrich Inc. (Bellefonte, PA, USA). A SPME holder was used to perform headspace SPME manually. SPME holders for manual sampling and fibre used in the analyses were purchased from Supelco Inc. (Bellefonte, PA, USA). SPME device included a fused silica fibre, partially cross-linked with 65 μm Carbowax/divinylbenzene (CW/DVB), which was conditioned according to the manufacturer's recommendations (250 °C for 30 min in the GC injector). The CW/DVB coating fibre was selected because it is a mixed coating that contains a liquid polymer and solid particles (Pillonel, Bossett, & Tabacchi, 2002). This type of coating combines the absorption properties of the liquid polymer with the adsorption properties of porous particles, which contains macro (>500 Å), meso (20–500 Å) and microporous (2–20 Å). The mutually synergetic effect of adsorption and absorption to the stationary phase promotes a high retention capacity and, consequently, a higher sensitivity than fibres based on absorption only. The CW/DVB coating fibre is recommended for smaller and polar molecules (molecular weight between 40 and 275 g/mol) and seems to be adequate for the analysis of complex matrices (Roberts, Pollien, & Milo, 2000; Song, Fan, & Beaudry, 1998), such as "Ameixa d'Elvas" plums.

2.3. SDE analysis

The "Ameixa d'Elvas" plums (±250 g, corresponding to 10 processed fruits), after removal of the stones, were immersed in distilled water (600 ml), and 100 μl of pentanoic acid (2 μl/ml) was added as internal standard. The samples were submitted to the volatile extraction in a modified Likens–Nickerson apparatus (Rocha, Delgadillo, & Correia, 1996; Schultz, Flath, Mon, Eggling, & Teranishi, 1977) for 3 h using bi-distilled dichloromethane (70 ml). After a few minutes of boiling extraction, an aqueous slurry of pulp was formed. The dichloromethane extracts were cooled to −20 °C to separate the frozen water from the organic phase by decantation and then the extracts were dried over anhydrous sodium sulphate. Each extract was concentrated to about 1 ml by distillation using a Vigreux column under low pressure at room temperature and a trap with liquid nitrogen on top. The concentrated extracts were stored in a glass screw-top vial at −20 °C until being analysed by GC–qMS. Three independent extractions were done and each extract was injected twice into the GC–qMS.

2.4. Headspace-SPME analysis

The "Ameixa d'Elvas" plums (60 ± 5 g, depending on their size, corresponding to 2–3 processed fruits), open in two halves, were placed into a 130 ml glass vial, which corresponds to a ratio of the volume of the solid phase to the headspace volume ($1/\beta$) of 0.5. The sucrose syrup (63 ± 3 g) was placed into a 130 ml glass vial, 8 g of NaCl was added to promote the salting out of the volatile compounds (results not shown), and the solution was stirred using a magnetic bar. The $1/\beta$ ratio was 0.5. The vials containing both types of samples (plum and syrup) were capped with a cap containing a butyl-rubber septum (Sigma-Aldrich Inc., Bellefonte, PA, USA) and placed in a thermostatted bath adjusted to 40.0 ± 0.1 °C to promote the transference of the compounds from the sample to the headspace. Two different times (60 and 120 min) of partition between the sample and headspace were tested. Partition time of 60 min between the sample and headspace was chosen for the analysis because no significant differences were observed in the chromatographic areas with increasing the time to 120 min (results not shown). After this step, the SPME fibre was

manually inserted into the sample vial headspace and the compounds were extracted for 45 min.

Blanks, corresponding to the analysis of the coating fibre not submitted to any extraction procedure, were run between sets of three analyses. All measurements were made with, at least, five replicates, being each replicate the analysis of one different aliquot (plum or syrup).

2.5. GC–qMS analysis

The dichloromethane extracts from SDE and the desorbed volatile compounds from SPME were separated and analysed on a GC–qMS, Agilent Technologies 6890N Network gas chromatograph. The GC was equipped with a 30 m × 0.32 mm (i.d.) DB-FFAP fused silica capillary column (J&W Scientific, Folsom, CA, USA), 0.25 μm film thickness, connected to an Agilent 5973 mass selective detector. Injections were made in splitless mode (5 min) and the injector was at 250 °C.

Some specific chromatographic conditions were used:

(i) For SDE, the volatile extract (1 μl) was injected in the injection port lined with a 4.0 mm i.d. splitless glass liner. The detector started to operate after 8 min of injection (solvent delay).
(ii) For SPME, the injection port was lined with a 0.75 mm i.d. splitless glass liner. The fibre, containing the headspace volatile compounds, was introduced into the injector for 5 min for desorption of the compounds. The detector started to operate immediately after the injection (no solvent delay).

The oven temperature was programed from 35 to 220 °C at 2 °C/min rate and the transfer line was heated at 250 °C. The helium carrier gas had a column head pressure of 12 psi. The mass spectrometer was operated in the electron impact mode at 70 eV, scanning the range *m/z* 30–300 in a 1 s cycle, in a full scan mode acquisition. Identification of volatile compounds was achieved by comparison of the GC retention times and mass spectra with those, when available, of the pure standard compounds. All mass spectra were also compared with the library data system of the GC–qMS equipment (Wiley 275).

Estimated concentrations for all compounds were made by GC peak area comparisons of the SDE extract components with the area of a known quantity of internal standard (pentanoic acid). The GC peak area data obtained by the HS-SPME analysis were used as an indirect approach to estimate the relative content of each volatile compound. The reproducibility of the results was expressed as the standard deviation in tables.

3. Results and discussion

3.1. Identification and quantification of "Ameixa d'Elvas" volatile composition

A total ion chromatogram of the SDE analysis of "Ameixa d'Elvas" plum is shown in Fig. 1a, with the attribution of peak numbers of the main components (shown in Table 1). This methodology allowed to identify and quantify seventy compounds, representing a total concentration of 49.4 mg/kg of pulp (Table 1). The acids, accounting for 22.6 mg/kg of pulp, represented the major group of compounds with 46% of the total concentration. From the 12 acids identified, hexadecanoic acid was the most abundant (16.5 mg/kg of pulp). Almost all other saturated even numbered straight chain fatty acids were also present: C_{14} (1.5 mg/kg), C_{12} (2.4 mg/kg), C_{10} (0.8 mg/kg), C_8 (0.3 mg/kg), C_6 (0.1 mg/kg), and C_2 (0.1 mg/kg), together with the odd numbered straight chain fatty acids C_{15} (0.5 mg/kg) and C_9 (0.2 mg/kg), the branched

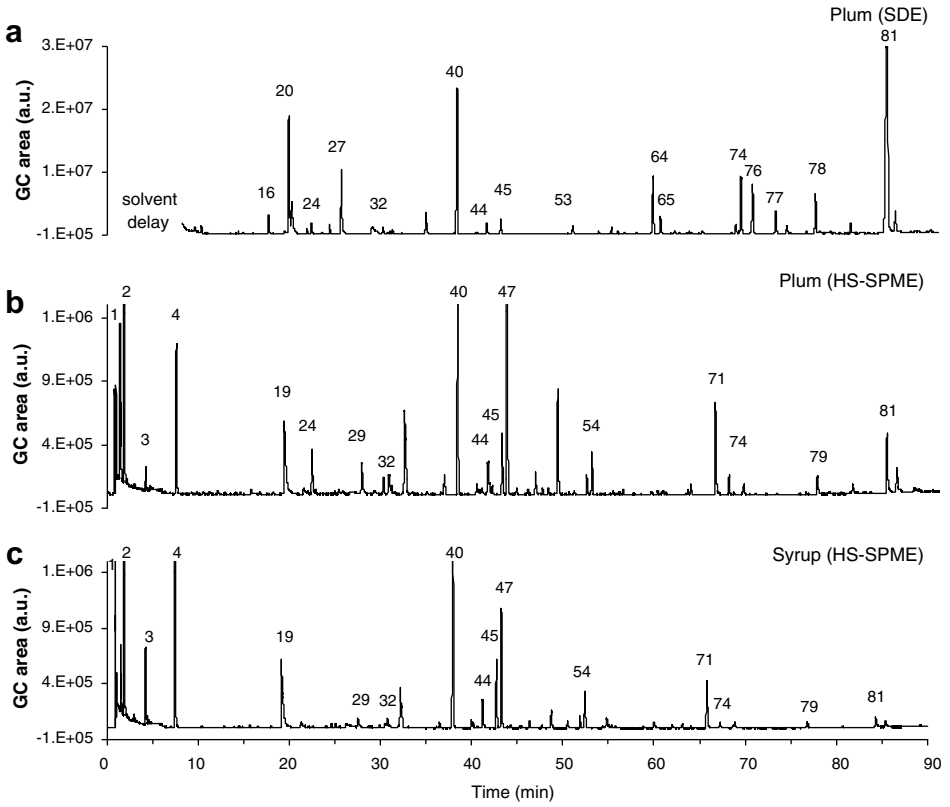

Fig. 1. Total ion chromatograms of the volatile compounds from "Ameixa d'Elvas" plums obtained by (a) SDE and (b) HS-SPME and from (c) sucrose syrup by HS-SPME (attribution of peak numbers of the main components shown in Table 1). a.u. – arbitrary units.

Table 1
Volatile composition of "Ameixa d'Elvas" plum identified by SDE and HS-SPME, and sucrose syrup by HS-SPME, grouped by chemical classes

Peak number	Compound	Identification [a]	Plum		Syrup	SPL[b] (μg/kg)
			SDE (μg/kg of pulp)	HS-SPME (area × 10^{-6})	HS-SPME (area × 10^{-6})	
	Acids					
19	Acetic acid	A, B, C	80.6 ± 9.4 [c]	73.5 ± 3.9 [d]	80.3 ± 2.3 [d]	60,000
34	3-Methyl butanoic acid	B, C	179.3 ± 5.9	tr[e]	tr	130
43	Hexanoic acid	A, B, C	129.3 ± 15.1	–	–	3000
50	2-Ethyl hexanoic acid	B, C	13.2 ± 1.9	–	2.2 ± 0.3	–
53	Octanoic acid	A, B, C	338.9 ± 39.5	2.9 ± 0.1	7.1 ± 1.5	3000
58	2,4-Hexadienoic acid	B, C	–	1.0 ± 0.1	2.5 ± 0.2	–
60	Nonanoic acid	A, B, C	188.3 ± 19.6	1.4 ± 0.1	2.3 ± 0.2	3000
66	Decanoic acid	A, B, C	822.5 ± 112.8	–	6.6 ± 0.4	10,000
71	Benzoic acid	B, C	21.8 ± 2.0	61.0 ± 3.2	36.4 ± 2.0	–
74	Dodecanoic acid	A, B, C	2404 ± 308	1.5 ± 0.4	2.5 ± 0.3	10,000
79	Tetradecanoic acid	B, C	1474 ± 153	72.0 ± 2.5	5.3 ± 0.7	10,000
80	Pentadecanoic acid	B, C	461.1 ± 38.0	–	–	10,000
81	Hexadecanoic acid	B, C	16484 ± 2648	49.5 ± 3.6	8.8 ± 0.5	10,000
	Subtotal (μg/kg or area × 10^{-6})		22596.6	262.8	154.0	
	Subtotal (%)		45.7	27.6	15.5	
	Alcanes					
41	Octadecane	B, C	23.1 ± 2.8	–	–	–
46	Nonadecane	B, C	47.2 ± 3.7	–	–	–
	Subtotal (μg/kg or area × 10^{-6})		70.3	–	–	
	Subtotal (%)		0.1	–	–	
	Alcohols					
2	Ethanol	B, C	–	144.4 ± 15.8	167.3 ± 8.0	10
3	2-Methyl-1-propanol	B, C	–	9.1 ± 0.5	22.3 ± 4.2	–
4	3-Methyl-1-butanol	B, C	22.4 ± 2.2	58.1 ± 3.8	100.2 ± 7.1	300
8	3-Methyl-2-buten-1-ol	B, C	16.6 ± 2.3	–	–	3
12	1-Hexanol	A, B, C	41.7 ± 4.7	–	0.8 ± 0.1	700
13	3-Ethoxy-1-propanol	B, C	31.5 ± 4.5	–	–	–
15	2-Butoxyethanol	B, C	38.2 ± 7.3	–	–	–
26	1-Octanol	A, B, C	43.5 ± 5.6	2.8 ± 0.1	3.5 ± 0.6	200
28	2,3-Butanediol	A, B, C	–	1.0 ± 0.1	3.3 ± 0.2	3
44	Benzyl alcohol	A, B, C	458.6 ± 67.7	20.5 ± 2.3	31.2 ± 6.0	20,000
45	2-Phenylethanol	A, B, C	424.6 ± 71.6	36.5 ± 1.7	66.3 ± 9.4	1100
67	3,7,11,15-tetramethyl-1-hexadecen-3-ol	B, C	44.0 ± 4.8	–	–	–
	Subtotal (μg/kg or area × 10^{-6})		1121.3	272.4	394.9	
	Subtotal (%)		2.3	28.6	39.8	
	Aldehydes					
1	Acetaldehyde	B, C	–	8.4 ± 0.3	3.4 ± 1.0	20
7	2-Heptenal	B, C	19.4 ± 2.2	1.6 ± 0.1	–	13
14	Nonanal	B, C	85.1 ± 8.9	2.6 ± 0.2	2.3 ± 0.3	1
21	Decanal	B, C	–	6.9 ± 0.5	6.4 ± 0.9	0.1
24	Benzaldehyde	A, B, C	728.2 ± 57.8	31.3 ± 2.0	tr	350
30	2,6,6-Trimethyl-1,3-Cyclo-hexadiene-1-Carboxaldehyde	B, C	21.6 ± 2.7	–	–	–
31	Phenylacetaldehyde	B, C	1378 ± 133	–	–	4
	Subtotal (μg/kg or area × 10^{-6})		2232.3	50.8	12.1	
	Subtotal (%)		4.5	5.3	1.2	
	Esters					
11	Ethyl 2-hydroxypropanoate	B, C	40.9 ± 3.4	–	–	–
18	Ethyl octanoate	A, B, C	40.1 ± 6.5	1.6 ± 0.1	1.6 ± 0.2	0.1
32	Ethyl benzoate	B, C	307.9 ± 47.2	12.3 ± 1.7	3.5 ± 0.3	60
37	Benzyl acetate	B, C	16.9 ± 3.2	–	–	360
38	Methyl 2-hydroxybenzoate	B, C	22.1 ± 3.4	–	–	–
40	2-Phenylethyl acetate	B, C	7635 ± 897	129.9 ± 11.8	277.8 ± 14.7	480
42	Ethyl dodecanoate	B, C	81.6 ± 9.4	–	–	5900
52	Ethyl tetradecanoate	B, C	67.3 ± 10.8	–	–	4000
62	Methyl hexadecanoate	B, C	67.3 ± 8.4	–	–	–
64	Ethyl hexadecanoate	B, C	2320 ± 224	–	–	2000
65	Dihydromethyl jasmonate	B, C	18.3 ± 2.3	1.1 ± 0.2	0.6 ± 0.2	–
70	Diethyl 1,2-Benzenedicarboxylate	B, C	109.7 ± 16.1	–	–	–
73	Ethyl heptadecanoate	B, C	104.5 ± 12.7	–	–	–
76	Ethyl linoleate	B, C	1723 ± 208	–	–	–
77	Ethyl linoleolate	B, C	779.6 ± 84.2	–	–	–
78	Dibutyl 1,2-Benzenedicarboxylate	B, C	133.8 ± 13.3	–	–	–
	Subtotal (μg/kg or area × 10^{-6})		13467.6	144.9	283.5	
	Subtotal (%)		27.2	15.2	28.6	

Table 1 (*continued*)

Peak number	Compound	Identification [a]	Plum		Syrup	SPL[b] (μg/kg)
			SDE (μg/kg of pulp)	HS-SPME (area × 10^{-6})	HS-SPME (area × 10^{-6})	
	Furans					
5	Dihydro-2-methyl-3(2H)-furanone	B, C	141.4 ± 6.8	–	–	–
16	5-Methyl-2(3H)furanone	B, C	771.4 ± 12.4	–	–	–
20	Furfural	A, B, C	4741 ± 496	–	–	3000
22	2,3,4-Trimethylfuran	B, C	51.6 ± 5.6	–	–	–
23	1-(2-Furanyl)-ethanone	B, C	260.7 ± 44.3	1.4 ± 0.2	0.9 ± 0.1	–
27	5-Methylfurfural	A, B, C	2777 ± 347	2.0 ± 0.1	–	–
29	Dihydro-2(3H)-furanone	A, B, C	–	28.2 ± 1.4	6.4 ± 0.3	–
33	Furfuryl alcohol	A, B, C	122.5 ± 11.8	4.2 ± 0.3	6.4 ± 0.2	–
56	Methyl 3-furancarboxylate	B, C	–	2.0 ± 1.0	–	–
75	5-Hydroxymethylfurfural	B, C	–	8.0 ± 0.4	4.8 ± 0.2	–
	Subtotal (μg/kg or area × 10^{-6})		8865.9	45.8	18.5	
	Subtotal (%)		17.9	4.8	1.9	
	Ketones					
6	3-Hydroxy-2-butanone	A, B, C	117.0 ± 12.5	–	–	–
9	2,3-Octanedione	B, C	19.9 ± 3.6	–	–	–
10	6-Methyl-5-hepten-2-one	B, C	17.6 ± 3.9	1.2 ± 0.2	0.8 ± 0.1	50
48	β-Ionone	A, B, C	59.3 ± 7.7	–	–	0.007
63	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	B, C	–	1.9 ± 0.1	–	–
72	Benzophenone	B, C	11.1 ± 0.6	–	–	–
	Subtotal (μg/kg or area × 10^{-6})		224.8	3.1	0.8	
	Subtotal (%)		0.5	0.3	0.1	
	Lactones					
57	γ-Decalactone	B, C	39.1 ± 5.3	–	–	11
68	γ-Dodecalactone	B, C	71.7 ± 9.5	–	–	7
	Subtotal (μg/kg or area × 10^{-6})		110.8	–	–	
	Subtotal (%)		0.2	–	–	
	Phenols					
47	2,6-Bis(1,1-dimethylethyl)-4-methylphenol	A, B, C	15.4 ± 1.6	150.8 ± 10.2	98.8 ± 17.2	–
49	2,3,6-Trimethylphenol	B, C	21.9 ± 2.9	–	–	–
51	Phenol	A, B, C	13.6 ± 1.9	4.5 ± 0.1	–	5900
55	2,6-Bis(1,1-dimethylethyl)-4-ethylphenol	B, C	–	3.8 ± 0.2	2.3 ± 0.2	–
59	2-Methoxy-4-(2-propenyl)phenol	A, B, C	278.4 ± 35.5	2.2 ± 0.3	5.3 ± 0.5	6
61	4-Vinyl-2-methoxy-phenol	B, C	78.5 ± 12.3	–	–	3
69	2,4-Bis(1,1-dimethylethyl) Phenol	B, C	50.6 ± 5.8	–	4.9 ± 0.9	–
	Subtotal (μg/kg or area × 10^{-6})		458.5	161.3	111.3	
	Subtotal (%)		0.9	16.9	11.2	
	Terpenoids					
17	*cis*-Linalool oxide	A, B, C	71.0 ± 11.3	–	–	320
25	Linalool	A, B, C	66.7 ± 5.1	1.7 ± 0.1	2.5 ± 0.3	6
35	α-Terpineol	A, B, C	66.7 ± 4.2	–	2.3 ± 0.3	330
39	β-Citronellol	A, B, C	10.8 ± 1.0	tr	1.2 ± 0.2	10
	Subtotal (μg/kg or area × 10^{-6})		215.1	1.7	6.0	
	Subtotal (%)		0.4	0.2	0.6	
	Others					
36	1,2-Dihydro-1,1,6-trimethylnaphthalene	B, C	38.8 ± 8.1	–	–	–
54	2-Formyl-1-methylpyrrole	B, C	27.9 ± 3.4	12.1 ± 1.4	11.0 ± 2.4	–
	Subtotal (μg/kg or area × 10^{-6})		66.7	12.1	11.0	
	Subtotal (%)		0.1	1.3	1.1	
	Total		49430	955	992	

[a] The reliability of the identification or structural proposal is indicated by the following: (A) mass spectra and retention time consistent with that of a standard; (B) structural proposal given on the basis of mass spectral data (Wiley 275); (C) mass spectrum consistent with spectra found in the literature.
[b] Sensory perception limit reported in the literature.
[c] Mean of six replicates (± standard deviation).
[d] Mean of five replicates (± standard deviation).
[e] tr – trace, detected by ion extraction analysis mode using specific *m/z*.

3-methyl butanoic acid (0.2 mg/kg) and 2-ethyl hexanoic acid (0.01 mg/kg), and benzoic acid (0.02 mg/kg of pulp). From these, only hexadecanoic acid and 3-methyl butanoic acid were above their sensory perception limits (SPL) of 10 and 0.13 mg/kg, respectively (Belitz et al., 2004). The fatty acids may arise from autoxidation of saturated lipids constituents of fruits, whose production was increased with the thermal treatment (Belitz et al., 2004).

The esters, accounting for 13.5 mg/kg of pulp, represented 27% of the total compounds. 2-Phenylethyl acetate (7.6 mg/kg) was the most abundant of the 16 esters recovered, and this compound was highly above its SPL (0.48 mg/kg) (Pino & Mesa, 2006). Also above their SPL (2.0, 0.06 and 0.0001 mg/kg, respectively) were ethyl hexadecanoate (2.3 mg/kg), ethyl benzoate (0.3 mg/kg) and ethyl octanoate (0.04 mg/kg) (Belitz et al., 2004; Pino, Marbot,

Rosado, & Vazquez, 2004). The esters are important aroma constituents of fruits, contributing to the fruity aroma notes. However, the processing promotes their hydrolysis and the fruity notes tend to be attenuated (Ismail et al., 1980b).

Representing 18% of the total compounds identified, and accounting for 8.9 mg/kg of the "Ameixa d'Elvas" plums, 7 furans were identified. Furfural was the major furan compound identified (4.7 mg/kg) and it was present in a concentration above its SPL of 3 mg/kg (Pino et al., 2004). Furans are formed from thermal degradation of sugars by caramelization, and they also arise from the decomposition of polysaccharides (Belitz et al., 2004; Rocha, Coimbra, & Delgadillo, 2004), thus their production occurred due to the high temperatures reached during processing of "Ameixa d'Elvas". However, part of this furan fraction may also occur as an artefact of the SDE methodology (Rocha et al., 1996). The use of an extraction methodology that does not include a thermal treatment, such as the SPME, can contribute to evaluate what are the compounds that can be considered mainly as SDE artefacts. Furan compounds were detected in some plum products that were submitted to high temperatures, such as prunes, canned plums, and jam (Crouzet et al., 1990).

Aldehydes accounted for 2.2 mg/kg of pulp, representing 4.5% of the total compounds quantified. Phenylacetaldehyde and benzaldehyde (1.4 and 0.7 mg/kg, respectively) were the most abundant aldehydes recovered. These compounds were above their SPL (0.004 and 0.35 mg/kg, respectively) (Belitz et al., 2004; Pino et al., 2004); also above their SPL were 2-heptenal (0.02 mg/kg) and nonanal (0.09 mg/kg), 0.01 and 0.001 mg/kg, respectively, (Pino & Mesa, 2006). Benzaldehyde has been already reported to increase on heating of fruits and/or making of jams (Belitz et al., 2004).

Alcohols, phenols, ketones, and alkanes accounted, respectively, for 1.1, 0.5, 0.2, and 0.1 mg/kg of pulp, representing together 3.8% of the total compounds. However, within these groups of compounds, 2-methoxy-4-(2-propenyl)phenol (0.3 mg/kg), 4-vinyl-2-methoxy-phenol (0.08 mg/kg), β-ionone (0.06 mg/kg), and 3-methyl-2-buten-1-ol (0.02 mg/kg) were above their SPL (0.006, 0.003, 0.000007, and 0.003 mg/kg, respectively) (Belitz et al., 2004; Pino et al., 2004; Pino & Mesa, 2006). The origin of C_6 alcohols, such as 1-hexanol, reported as an important contributor to the aroma of the fresh plums (Crouzet et al., 1990; Williams & Ismail, 1981), are related to the lipoxygenase activity. This enzyme that occurs in plants and, namely, in fruits catalyses the oxidation of unsaturated fatty acids (Belitz et al., 2004), as a first step to the production of compounds such as the short chain alcohols. The C_6 alcohols contribute to green and herbaceous notes. Some phenols have been also related with the heat processed aroma of the plums. Their origin was explained by thermal degradation of precursors like phenolic acids (Crouzet et al., 1990; Ismail et al., 1980b; Sabarez, Price, & Korth, 2000).

Terpenoids accounted for 0.2 mg/kg, representing only 0.4% of the total compounds identified. From these, linalool (0.07 mg/kg) was above its SPL (0.006 mg/kg). In this group, β-citronellol was recovered in a concentration similar to its SPL of 0.01 mg/kg (Belitz et al., 2004). The terpenoids, namely the monoterpenols, were reported as volatile components of fruits responsible for a wide spectrum of aromas, mostly perceived as very pleasant (Belitz et al., 2004; Coelho, Rocha, Delgadillo & Coimbra, 2006). These compounds are responsible to the varietal character of the fruits, being present, at least in part, as glycosides (Belitz et al., 2004). Linalool, already identified in fresh plums (Crouzet et al., 1990; Williams & Ismail, 1981), as well as *cis*-linalool oxide, α-terpineol, and β-citronellol may arise, at least in part, due to the hydrolysis of the corresponding glycosides promoted by the heat processing.

γ-Dodecalactone and γ-decalactone, which accounted for 0.07 mg/kg and 0.04 mg/kg, were above its SPL of 0.007 mg/kg and 0.01 mg/kg, respectively (Engel, Flath, Buttery, Mon, Ramming & Teranishi, 1988). Lactones are formed from the corresponding hydroxy acids. These compounds, particularly γ-lactones, are important compounds in terms of their contribution to the aroma and, in general, present fruity odour descriptors.

3.2. Establishment of the headspace volatile profile of "Ameixa d'Elvas"

3.2.1. Headspace volatile composition of "Ameixa d'Elvas" plums

In order to determine the headspace volatile profile of "Ameixa d'Elvas", SPME technique was used. Fig. 1 shows the total ion chromatogram of volatile compounds for "Ameixa d'Elvas" plums obtained by SPME (Fig. 1b). Forty compounds were identified as shown in Table 1. Excluding the alkanes, compounds representative of all the other chemical groups detected by SDE were also detected by HS-SPME. Alcohols (29% of the compounds) and acids (28%) represented the principal chemical groups.

A qualitative comparison between the SDE and HS-SPME data indicates that the higher differences were observed for the esters, furans, ketones, and terpenoids, present in higher number in the SDE data set. These results may be explained based on the peculiarities of each extraction procedure used. The SPME is a non-exhaustive extraction methodology that also combines the sampling and pre-concentration steps. The SPME experimental parameters should be optimised and controlled to guarantee that a proportional relationship is obtained between the amount of the analyte extracted by the SPME fibre and its initial concentration in the sample matrix (Kleeberg, Dobberstein, Hinrichsen, Müller, Weber, & Steinhart, 2007, chap. 13). The SDE represents an exhaustive extraction methodology. In this case, the plum was dispersed as a pulp in hot water and extracted with dichloromethane for 3 h, promoting a high area of contact with the solvent. Consequently, an extraction of a higher number of compounds was obtained than using SPME. Furthermore, the conditions of the SDE analysis, namely the temperature, may provoke artefacts. For example, β-ionone, a ketone, is a C_{13}norisoprenoid compound that arises from carotenoids. It has been reported for other fruits, such as grapes, that glycosylation of norisoprenoids may occur during ripening of the fruit. Therefore, a decrease of these compounds in free form was expected (Baumes, Wirth, Bureau, Gunata, & Razungles, 2002). However, the results obtained suggest that during the SDE, the reactions originating the β-ionone (hydrolysis of the glycosidic precursor, reduction of *Grasshopper ketone*, dehydration...) (Belitz et al., 2004) have occurred. This may explain the recovery of β-ionone by SDE and its absence in the headspace analysed by HS-SPME. In what concerns the furans, it was assumed that the compounds recovered only by the SDE, such as dihydro-2-methyl-3(2H)-furanone, 5-methyl-2(3H)furanone, furfural, and 2,3,4-trimethylfuran were formed mainly during the SDE extraction, and were considered as SDE artefacts. The other furans recovered by SDE and also present in the headspace, given by the HS-SPME data, may have been produced due to the high temperatures reached during the candying process of "Ameixa d'Elvas".

On the other hand, the HS-SPME allows the detection of the low boiling point volatiles that overlap with the solvent in the SDE. Thus, acetaldehyde, ethanol, and 2-methyl-1-propanol could only be detected by HS-SPME, since they appear in the retention times that are included in the solvent delay. The occurrence of ethanol led to the possibility that fermentation had occurred. This hypothesis is also suggested by the presence of 2-methoxy-4-(2-propenyl)phenol (eugenol), acetic acid, and several ethyl esters quantified by SDE. Eugenol arised from the corresponding phenolic alcohol or from ferulic acid during fermentation (Crouzet et al., 1990), compounds also found in fermented plum brandies (Ismail, Williams, & Tucknott, 1980a).

In the HS-SPME analysis, the "Ameixa d'Elvas" plum was cut into two halves and the intact plum was analysed. This allowed

to simulate the state of the plum when it is consumed, releasing only the volatiles that potentially contribute to its aroma as are perceived by the consumers. As the intact plum may retain the volatiles, not being released to the headspace, the number of compounds (even the quantity, but this was not the aim of the present study) that may be recovered in the headspace should be lower than that obtained by SDE.

3.2.2. Headspace volatile composition of "Ameixa d'Elvas" sucrose syrup

In order to evaluate the contribution of the 75 °Brix syrup used in the storage of "Ameixa d'Elvas" plums to the overall aroma of the product, it was analysed by HS-SPME using the experimental conditions already used for the analysis of the plums headspace. Considering the chemical composition of the syrup, the SDE should not be adequate to its analysis, since it promotes a high level of furans.

Fig. 1c shows the total ion chromatogram of the volatile compounds for "Ameixa d'Elvas" syrup. In "Ameixa d'Elvas" syrup 40 compounds were identified (Table 1). All the chemical groups detected in the plum by HS-SPME were also detected in the syrup. Alcohols and esters represented the principal chemical groups, with 40% and 29% of the compounds, respectively. Although with different relative GC peak areas, generally, the compounds identified in the fruits were also identified in the syrup (Table 1), indicating the diffusion of the volatile components from the fruits to the syrup during their processing and storage. It is also important to highlight that in the syrup there were detected more terpenoids (linalool, α-terpineol, and β-citronellol) than in the fruit headspace, which suggests the capacity of the syrup to retain and concentrate these compounds. As the fruit can also be consumed with the syrup, this result advises its potential contribution to the preservation of the aroma character of "Ameixa d'Elvas".

3.3. Estimation of the contribution of the "Ameixa d'Elvas" volatiles to the aroma

3.3.1. Identification of the compounds with aroma indexes higher than 1

Calculations of aroma indexes (I) are necessary to obtain a more accurate estimation of the contribution of the compounds to the aroma of "Ameixa d'Elvas". For this purpose, the aroma potential of each compound was assessed by calculating the aroma index ($I = c/s$ where c is the concentration found in the plum pulp by SDE and s is the SPL for the compound reported in the literature).

The SPL vary depending on the sample matrix, pH, sample temperature, and the methodologies of sensory analysis used. Therefore, comparisons of aroma contribution on I are very difficult when SPL from different sources are used. However, in this study, SPL in water were used for all the compounds available because there is no data available for candied fruit matrices, although, ideally, the SPL should have been determined for "Ameixa d'Elvas" (Grosch, 2001; Qian & Reineccius, 2003). The use of SPL determined in a model medium (water) ignores the influence of the fruit components on the release of odourants. Despite these limitations, the I concept is still considered a very useful tool in aroma research studies (Belitz et al., 2004; Stephan, Bücking, & Steinhart, 2000).

Compounds that exhibit $I > 1$ are considered to have a potential individual contribution to the aroma. Furthermore, according to Meilgaard's suggestion of the sensory contribution to the overall aroma of a substance, when its concentration is at least 20% of the threshold unit ($I > 0.2$), it should be considered (Belitz et al., 2004).

In "Ameixa d'Elvas", 19 compounds were identified as having an $I > 1$ (Table 2):

Table 2
Aroma index (I) of the volatile compounds of "Ameixa d'Elvas" plum with $I > 1$ and their odour descriptor (from the literature) with Indication of their detection by HS-SPME in plum and sucrose syrup

Compound	I	Odour descriptor	HS-SPME	
			Plum	Syrup
β-Ionone	8429	Violet, sweet, fruity, berry	–	–
Ethyl octanoate	400	Pleasant, cooked, fruity	×	×
Phenylacetaldehyde	345	Green, pungent	–	–
Nonanal	85	Sweet, fruity	×	×
2-Methoxy-4-(2-propenyl)phenol (eugenol)	46	Sweet, phenolic	×	×
4-Vinyl-2-methoxy-phenol	26	Clove-like	–	–
2-Phenylethyl acetate	16	Fruity, rose	×	×
Linalool	11	Sweet, floral	×	×
γ-Dodecalactone	10	Peach, apricot	–	–
3-Methyl-2-buten-1-ol	5.5	Apple	–	–
Ethyl benzoate	5.1	Fruity	×	×
γ-Decalactone	3.6	Peach, apricot, nectarine	–	–
Benzaldehyde	2.1	Sweet, fruity	×	×
2-Heptenal	1.9	Sweet, fruity	×	–
Hexadecanoic acid	1.6	Grassy, heavy	×	×
Furfural	1.6	Toasty, burnt	–	–
3-Methyl butanoic acid	1.4	Harsh, pungent	×	×
Ethyl hexadecanoate	1.2	Peppery	–	–
β-Citronellol	1.1	Fruity	×	×

- β-ionone was found as having the highest aroma index value ($I = 8429$), and to exhibit a violet-like odour, although it is also associated with sweet, fruity and berry descriptors in tropical fruits (Mahattanatawee, Goodner, & Baldwin, 2005; Pino & Mesa, 2006);
- ethyl octanoate ($I = 400$), 2-phenylethyl acetate ($I = 16$), ethyl benzoate ($I = 5$) and ethyl hexadecanoate ($I = 1$) have been described to have aroma descriptors of, respectively, pleasant cooked fruity (Fang & Qian, 2005), fruity rosy, fruity (Pino & Mesa, 2006), and peppery (Chisholm, Wilson, & Gaskey, 2003);
- 3-methyl-2-buten-1-ol was the only alcohol detected that exhibits an aroma index >1 ($I = 6$) and it may contribute individually with apple notes (Boulanger & Crouzet, 2000);
- γ-dodecalactone had an I of 10 and it is associated with peach and apricot descriptors (Engel et al., 1988), and γ-decalactone, with an I of 4, is associated with peach, apricot, and nectarine descriptors (Engel et al., 1988);
- furfural was detected with an I of 2, which could contribute individually with toast and burnt notes (Fang & Qian, 2005);
- nonanal ($I = 85$) and benzaldehyde ($I = 2$) have been described as contributors to the aroma of the fresh plums (Williams & Ismail, 1981), as well as major constituents of canned plums and jams. All these compounds, as well as 2-heptenal ($I = 2$), are associated with sweet, fruity, and floral odours (Mahattanatawee et al., 2005). In addition, phenylacetaldehyde, which showed a high aroma index ($I = 345$) has been described as having a green pungent odour (Mahattanatawee et al., 2005);
- linalool ($I = 11$) and β-citronellol ($I = 1$) exhibit sweet, floral and fruity odours (Fang & Qian, 2005);
- 2-methoxy-4-(2-propenyl)phenol ($I = 46$) and 4-vinyl-2-methoxyphenol ($I = 26$), have aroma descriptors of, respectively, sweet phenolic (Miranda, Nogueira, Pontes, & Rezende, 2001; Sabarez et al., 2000) and clove-like (Belitz et al., 2004);
- hexadecanoic acid ($I = 2$) has been described to have grassy and heavy descriptors (Boulanger & Crouzet, 2000), and 3-methyl butanoic acid ($I = 1$) has been described as harsh and pungent in fruits (Miranda et al., 2001; Sabarez et al., 2000).

3.3.2. Searching the would-be impact odourants

HS-SPME headspace technique was used to evaluate if the volatile compounds identified as having $I > 1$ were present in the headspace of the plums. As the molecules present in the headspace are indeed responsible for the smell that is perceived by the olfactory system, if they are in concentrations above their SPL, these compounds are considered to be potential contributors to the aroma of the "Ameixa d'Elvas" and can be designed as would-be impact odourants.

From the 19 compounds that exhibit an $I > 1$, 11 were detected in "Ameixa d'Elvas" plums by HS-SPME: ethyl octanoate, nonanal, 2-methoxy-4-(2-propenyl)phenol, 2-phenylethyl acetate, linalool, ethyl benzoate, benzaldehyde, 2-heptenal, hexadecanoic acid, 3-methyl butanoic acid, and β-citronellol (Table 2). Therefore, these are the would-be impact odourants of "Ameixa d'Elvas". Almost all these compounds are associated with sweet, cooked and fruity odours (Table 2). The other eight compounds determined to have an $I > 1$ and that were not detected in the fruit headspace by HS-SPME were probably retained in the fruit, not being released to the headspace of the "Ameixa d'Elvas".

Excluding the 2-heptenal, all the established would-be impact odourants of "Ameixa d'Elvas" were also detected in the syrup headspace (Table 2). Retention of volatile compounds, namely linalool, has been shown to occur in sucrose/pectin-rich matrices, although no interaction has been observed for ethyl esters (Savary, Guichard, Doublier, & Cayot, 2006). Also, high methoxyl pectins have been shown to cause a decrease in the amount of volatile compounds detected in the headspace in jams (Guichard, Issanchou, Descourvieres, & Etievant, 1991). "Ameixa d'Elvas" syrup is composed by 1% polysaccharides, mostly pectic polysaccharides with a mean degree of esterification of 68% (results not shown). This allows expecting retention of volatiles in the sucrose syrup matrix. However, syrup could have an opposite effect, because increasing concentrations of sucrose enhance the release of volatile compounds to the headspace (Nahon, Harrison, & Roozen, 2000; Nahon, Koren, Roozen, & Posthumus, 1998). The release of the compounds to the syrup headspace depends on the equilibrium between these effects, as well as on the physico-chemical properties of the compounds.

4. Conclusion

The present study allowed to establish the volatile composition of "Ameixa d'Elvas", which includes 10 chemical groups: acids, esters, furans, aldehydes, alcohols, phenols, ketones, terpenoids, lactones, and alkanes. This composition reflects the complexity of the reactions (enzymatic or not) and rearrangements that happen during the fruit ripening plus those occurring due to the thermal processing of the fruit in the presence of sucrose. "Ameixa d'Elvas" contains volatile compounds that arise from different origins: (i) characteristic from the fruit (acids, terpenoids, lactones, and esters), (ii) produced during the heat processing (furans and compounds released from the glycosidic precursors), and (iii) compounds that seems to indicate the occurrence of fermentation (ethanol, eugenol, esters, and acetic acid). Some compounds have more than one origin.

The approach applied to obtain these results included the use of: (i) SDE, that promoted an exhaustive extraction of the pulp dispersed in hot water, allowing a deep analysis of the volatile fraction of "Ameixa d'Elvas" and the determination of the compounds with $I > 1$, and (ii) HS-SPME, allowing to detect the volatile compounds present in the headspace of the intact pulp, and potentially responsible for the aroma properties. From the 19 compounds that exhibit an $I > 1$, 11 compounds were detected in "Ameixa d'Elvas" plums by HS-SPME: ethyl octanoate, nonanal, 2-methoxy-4-(2-propenyl)phenol, 2-phenylethylacetate, linalool, ethyl benzoate, benzaldehyde, 2-heptenal, hexadecanoic acid, 3-methyl butanoic acid, and β-citronellol. Therefore, these are the would-be impact odourants of "Ameixa d'Elvas", which are associated with sweet, cooked, and fruity odours. Excluding 2-heptenal, all the established would-be impact odourants of "Ameixa d'Elvas" were also detected in the syrup headspace. The present study also indicated the occurrence of transference of volatile components from the processed fruits to the syrup during storage, revealing the capacity of the syrup to retain and concentrate these compounds. As the fruit can also be consumed with the syrup, this result advises to its potential contribution to the preservation of the aroma character of "Ameixa d'Elvas" candied plums.

This methodology that comprises the combination of the analysis of SDE-GC–qMS and HS-SPME–GC–qMS data seems to be suitable to characterise the volatile fraction as well as to estimate its contribution to the aroma properties of heat treated fruits. However, as a preliminary study, these features need confirmation using a sensory panel and/or GC–olfactometry. The approach proposed in this study can be extended to the analysis of other solid matrices.

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