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A study of volatile flavour substances in Dalmatian traditional smoked ham: Impact of dry-curing and frying

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Abstract

Volatiles from Dalmatian prosciutto were isolated by solvent extraction (SE), simultaneous distillation extraction (SDE) and nitrogen purge and steam distillation (NPSD) and analyzed by GC and GC–MS. In all, 46 compounds were identified by SDE and SE (including fatty acids, aldehydes, phenols, esters, ketones and others), while 81 compounds were identified by NPSD (headspace volatiles including phenols, aldehydes, hydrocarbons, ketones, alcohols, esters and heterocyclic compounds). Regarding the impact of dry curing period on the volatiles, an increase in the percentages of aldehydes and esters during the ripening of the prosciutto was observed. Quantitative percentage differences among fried and raw samples were particularly evident in respect of aldehydes (SDE and SE). The NPSD method provided additional information of the volatiles from fried ham, since the pyrazines and most of the lower aldehydes that are important thermally derived flavour compounds were only isolated by NPSD (not by SE and SDE).

Keywords: Smoked ham; Fried ham; Prosciutto; Volatiles; Simultaneous distillation extraction (SDE); Solvent extraction (SE); Nitrogen purge and trap distillation (NPSD)

1. Introduction

Smoked and dry-cured ham (prosciutto) from Dalmatia (southern part of Croatia) is a famous specialty with excellent international consumer acceptance. Although prosciutto is mainly consumed raw, it is also served as cooked or fried ham. Traditional Dalmatian prosciutto is made by salting, pressuring, smoking and dry-curing for 12–24 months without any additives such as nitrites or ascorbic acid. Its flavour is the most important attribute and it is known to differ from other famous south European hams that are made by salting and dry-curing (Dirinck, Van Opstaele, & Vandendriessche, 1997; Sabio, Vidal-Aragón, Bernalte, & Gata, 1998).

It is known that during the processing of dry-cured ham numerous enzymatic and non-enzymatic reactions occur such as protein degradation, lipid degradation and oxidation, Maillard reactions and Strecker degradation. These changes give rise to volatile compounds such as aldehydes, carboxylic acids, alcohols, ketones, esters, sulphur and nitrogen compounds, terpenes, alkanes and alkenes, aromatic and cyclic hydrocarbons (Dirinck et al., 1997; Mottram, 1998; Sabio et al., 1998; Toldrá, 1998; Vestergaard, Schivazappa, & Virgili, 2000). The composition and quantity of these volatiles in different hams are affected by the length of the curing process resulting in a variety of flavour tones (Andrés, Cava, & Ruiz, 2002; Ruiz, Ventanas, Cava, Andrés, & Garciá, 1999). In spite of to the negative effect of lipid oxidation, the typical aroma of dry-cured ham is related to the initiation of lipid oxidation and the subsequent generation of volatiles (Buscailhon, Berdagué, & Monin, 1993). Smoke-cured ham also contains low-molecular-weight phenol derivatives (lignin monomer derivatives) derived from the smoke or smoke flavourings produced during lignin pyrolysis (Ai-Nong & Bao-Guo, 2005; Guillén & Ibargoitia, 1999). Unfortunately, some polycyclic aromatic hydrocarbons (PAH) can originate

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from smoke that are cancer causing agents, or if not carcinogenic, they may act as synergists (Šimko, 2002).

Frying is used to develop desirable sensory properties of foods correlated to colour, flavour, texture, and palatability. During frying, various chemical processes occur including oxidation, polymerization, isomerization, cyclization and hydrolysis (Gertz, 2000). For example, the main reactions during frying of bacon resulting in the formation of aroma volatiles are sugar degradation and/or Maillard reactions and the thermal degradation of lipids (Timón, Carrapiso, Jurado, & van de Lagemaat, 2004). Identified volatile compounds from fried bacon samples include hydrocarbons, alcohols, ketones, aldehydes, acids, esters, phenols, pyrazines, furans, thiazoles, oxazoles, pyrroles, pyridines, etc. (Ho, Lee, & Jin, 1983; Timón et al., 2004), many of which are secondary oxidation products. Such mixtures of components arising at different frying temperatures give very complex flavour profiles. Various aldehyde species, i.e. (*E*)-2-alkenals, (*E*,*E*)-alka-2,4-dienals and *n*-alkanals, arise from the fragmentation of conjugated hydroperoxy-diene precursors and have been associated with cytotoxic effects on experimental animals (Witz, 1989).

Different analyses techniques such as steam distillation, simultaneous distillation extraction, headspace solid phase microextraction, solvent extraction, purge and trap distillation and supercritical CO_2 extraction have been used to analyse the volatile flavour compounds from foods leading to different results (Carrapiso, Ventanas, & García, 2002; Mariaca & Bosset, 1997; Timón, Ventanas, Martín, Tejeda, & García, 1998; Wilkes et al., 2000). Although the higher-molecular fat derived compounds have a high perception threshold, they play a small but direct role in total perceived flavour. However, for the elucidation of the pathways for the formation of the lower-molecular weight compounds, detection of all fat-derived compounds is valuable.

Therefore, the aim of the present research work was to identify, for the first time, the volatile flavour compounds present in autochthonous Dalmatian traditional smoked and dry-cured ham, as well as to investigate their general trend with respect to the dry-curing period and during frying. The isolation of the volatiles is carried out by solvent extraction (SE), simultaneous distillation extraction (SDE) and nitrogen purge and trap distillation (NPSD). Gas chromatography coupled to mass spectrometry (GC–MS) is used for the analyses of the isolated volatiles. These results may be helpful as a tool for the certification of this autochthonous Croatian food product.

2. Materials and methods

2.1. Material and reagents

Dalmatian smoked and dry-cured ham (prosciutto) was obtained from a local food manufacture (Gradina, Studenci, Croatia). The samples were moderately salted, and had a dark red colour with recognizable aroma. The prosciutto had been prepared according to the traditional processing procedures without any additives such as nitrites or ascorbic acid being added. Traditional processing of Dalmatian ham starts in December, when the raw ham is placed in sea salt at a temperature of 10–12 °C. After 12 days, the ham is drained off and smoked for five days and then pressed (for removal of water) under a constant pressure of cca. 0.1 kg cm^{-2} for two days. Thereafter, the ham is smoked with dry hornbeam wood for 20 days and pressured again under a constant pressure of cca. 0.17 kg cm^{-2}. The ham is then dried under normal environmental conditions (cold and dry north-eastern wind is important) with occasionally smoking until March, and left for further drying until May. The relative humidity (60–70%) during the processing depends on the climatic conditions. The ham is further moved to a cellar for ripening at mild temperatures (12–15 °C) until consumption. The ripening period (before consumption) is usually 12–24 months. The hams are from pigs of the same feedlot with similar feed. Samples were taken from biceps femoris muscle from the hams. Three batches of each sample with different dry-curing periods (since beginning of drying under normal environmental conditions) were investigated: 60 days (sample A), 365 days (sample B) and 910 days (sample C). After removal of the dust and subcutaneous depot fat the samples were cut into thin pieces. Sample B presents the age period when prosciutto is most often consumed, and a sub-sample of B (75 g) was pan fried at approximately 200 °C for 3 min and investigated as fried prosciutto (marked as sample D). All of the solvents employed (p.a. grade), anhydrous sodium sulfate, 1,2-dichlorobenzene and other reference compounds were purchased from Fluka Chemie (Buchs, Switzerland). Ether was dried over K_2CO_3 and distilled. Oxygen free nitrogen gas was purchased from Messer, Dugi Rat, Croatia.

2.2. Solvent extraction (SE)

Each sample (20 g) was exhaustively extracted in a Soxhlet apparatus with diethyl ether for 12 h at 40 ± 5 °C. The ether extract was dried over anhydrous sodium sulfate and concentrated by fractional distillation to a volume of 10 mL. The extracts were kept for 20 min in tubes at −4 °C for successive precipitation of the triglycerides. After cold centrifugation (2000*g*, 3 min), the top layer was transferred to another tube and kept at −20 °C for 30 min. Additional precipitated triglycerides were discarded after a brief centrifugation (2500*g*, 10 s), and 1 mL of the supernatant was then transferred into a GC-vial for GC and GC–MS analysis.

2.3. Simultaneous distillation extraction (SDE)

The volatiles were isolated from 75 g of each sample by simultaneous hydrodistillation (cca. 100 °C) and extraction in a Likens–Nickerson apparatus (Likens & Nickerson, 1964). The isolation was performed for 2.5 h with solvent pentane/ether (1:1 v/v). The pentane/ether extract was

dried over anhydrous sodium sulfate and concentrated by fractional distillation up to volume of 1 mL for GC and GC–MS analysis.

2.4. Nitrogen purge and steam distillation (NPSD)

The apparatus for NPSD comprised of a 100 mL two-neck flask for the inlet of the purging nitrogen gas and for outlet of the nitrogen containing the purged volatiles, the later was connected to the cold traps (Ai-Nong & Bao-Guo, 2005; Ramarathnam, Rubin, & Diosady, 1993). The sample (65 g) was placed in the flask where it was constantly maintained at 102 ± 5 °C with the use of an oil bath. A slow stream of nitrogen was passed through the sample to purge the volatiles from the headspace. The effluent stream was condensed through a series of cold traps. The first cold trap (first trap) was maintained at a temperature of 2–4 °C with crushed ice; the second cold trap (second trap), containing 30 mL of ether, was maintained at −20 °C with an ice–$CaCl_2$ mixture; and the third cold trap (third trap), containing 30 mL of *n*-pentane, was also maintained at −20 °C with the ice–$CaCl_2$ mixture. The volatiles were collected over a 10 h purging and distilling period. At the end of the experiment, the volume of the condensate collected at the first cold trap was cca. 30 mL. This condensate was extracted twice with 30 mL diethyl ether. The ether extracts were combined, dried over anhydrous sodium sulfate and concentrated by fractional distillation to a final volume of 0.2 mL. The extracts from the second and the third cold trap were also dried and concentrated by fractional distillation up to 0.2 mL. All the concentrates were analyzed by GC and GC–MS.

2.5. Gas chromatography (GC) analysis

Gas chromatography analyses were performed on a Hewlett–Packard model 5890 series II gas chromatograph equipped with flame ionization detector and a capillary column HP-101 (polydimethylsiloxane, Hewlett–Packard, Vienna, Austria), 25 m × 0.2 mm i.d. with coating thickness 0.2 μm. Chromatographic conditions were as follows: helium as carrier gas at 1.0 mL min^{-1}; injector and detector temperatures, 250 °C and 300 °C. Oven temperature was isothermal at 70 °C for 2 min, then increased to 200 °C at a rate of 3 °C min^{-1} and held isothermal for 15 min. The volume injected was 1 μL and the split ratio was 1:50.

2.6. Gas chromatography–mass spectrometry (GC–MS) analysis

The analyses were performed on a GC–MS Hewlett–Packard (model 5890 with a mass selective detector model 5971A, Hewlett Packard, Vienna, Austria) using a HP-101 column (polydimethylsiloxane, Hewlett Packard, Vienna, Austria), 25 × 0.2 mm i.d. with a film thickness 0.2 mm. The oven temperature was programmed as follows: 70 °C isothermal for 2 min, then increased to 200 °C at a rate of 3 °C min^{-1} and held isothermal for 15 min. The carrier gas was helium with a flow rate 1.0 mL min^{-1}. The injector temperature was 250 °C. The volume injected was 1 μL and the split ratio was 1:50. MS conditions were: ionization voltage 70 eV; ion source temperature 280 °C; mass range 30–300 mass units. The conditions for the chromatographic separation and mass spectrometry have been used as described previously (Jerković & Mastelić, 2003).

2.7. Identification and quantitative determination of components

The individual peaks were identified by comparison of their retention indices (relative to C_9–C_{22} *n*-alkanes) to those of authentic samples (series of alkanes, alcohols, aldehydes, acids and some phenols) and literature data (Adams, 1995; Ramarathnam et al., 1993; Timón et al., 2004), as well as by comparing their mass spectra with the Wiley 6.0 library (Wiley, New York) and NIST98 (National Institute of Standards and Technology, Gaithersburg) mass spectral database. Determination of the percentage composition was based on peak area normalization without the use of correction factors. The content of isolated volatiles for three batches of each sample was calculated from GC peak areas related to the GC-peak area of 1,2-dichlorobenzene (internal standard) in duplicate GC-analyses. Preliminary GC–MS analysis indicated the absence of 1,2-dichlorobenzene among the isolated volatiles. Total amount of isolated volatiles is expressed in terms of milligrams per kilogram of the individual sample. The component percentages in Tables 1 and 2 were calculated as the mean-value of duplicate GC and GC–MS analyses for three batches of each sample showing the general trend of isolated volatiles with respect to the dry-curing period and frying.

3. Results and discussion

The flavour volatiles (as key quality characteristic) of Dalmatian ham from all the samples (A–D) were isolated by simultaneous distillation extraction (SDE), with yields from 41.5 mg kg^{-1} up to 74.4 mg kg^{-1} (Table 1), by solvent extraction (SE) using ether with yields from 278.8 mg kg^{-1} up to 330.2 mg kg^{-1} (Table 1) and by nitrogen purge and trap distillation (NPSD) with overall yields from 4.4 mg kg^{-1} up to 15.6 mg kg^{-1} (Table 2). The amount of isolated volatiles extracted by SE was higher, most probably due to the exhaustive extraction of the medium volatile compounds that are partially isolated by SDE. The NPSD method extracts only headspace volatiles and the yields obtained were lower than that from the SE and SDE methods.

In total 35 compounds (Table 1) were identified, by means of GC and GC–MS, in the samples (A–D) using SDE, whereas 37 were detected in the SE extracts. The SDE isolation method was applied by boiling the sample in water which mimics the cooking process of ham whilst

simultaneously isolating the volatiles. However, the use of SDE can produce artefacts from oxidation and thermal reactions (Chaintreau, 2001). Heavy components (semi-volatile) and volatile components were isolated using the SE method at 40 ± 5 °C, and it should be taken into consideration that some remaining non-volatile material in the SE extract may also generate artefacts in the GC injector.

Table 1
Medium and low-volatile compounds in samples A–D of Dalmatian smoked and dry-cured ham isolated by simultaneous distillation extraction (SDE) and solvent extraction (SE)

	RI (HP-101)	Percentage[a] (%)							
		Sample C		Sample B		Sample A		Sample D	
		(SDE)	(SE)	(SDE)	(SE)	(SDE)	(SE)	(SDE)	(SE)
1. 3-Butenoic acid	836	–	–	–	0.9	–	0.4	–	0.3
2. Butanoic acid	880	–	0.6	–	0.5	–	0.4	–	0.2
3. Furfuryl alcohol	920	0.6	0.3	0.2	0.1	–	–	–	–
4. (*E*)-2-Heptenal	922	–	0.2	–	0.2	–	–	–	–
5. Pentanoic acid (*Valeric acid*)	933	–	0.4	–	0.4	–	0.2	–	0.2
6. 2-Pentylfuran	966	1.3	–	–	–	–	–	0.2	0.3
7. Phenylacetaldehyde	1025	5.0	0.2	0.3	–	0.2	–	0.4	0.2
8. Nonanal	1072	1.5	–	–	–	–	–	0.3	0.2
9. Hexanoic acid	1083	–	0.3	–	0.9	–	–	–	0.2
10. Benzyl alcohol	1092	–	–	–	–	0.1	–	0.1	–
11. 2-Methoxyphenol (*Guaiacol*)	1116	0.9	–	0.5	0.2	0.3	–	0.2	–
12. Phenol	1137	2.6	0.2	1.0	0.4	0.4	0.1	0.2	0.1
13. 2-Methylphenol (*o-Cresol*)	1166	0.6	–	0.5	0.2	0.2	–	0.2	–
14. 3-Methylphenol (*m-Cresol*)	1205	2.4	–	1.2	0.4	0.5	–	0.3	0.1
15. (*E*)-2-Decenal	1232	2.8	4.9	–	2.4	–	0.4	1.2	3.1
16. 2,5-Dimethylphenol (*2,5-Xylenol*)	1246	–	–	0.2	–	0.2	–	–	–
17. Octanoic acid *(Caprylic acid)*	1262	–	–	–	0.5	–	–	–	–
18. (*E*,*Z*)-2,4-Decadienal	1268	3.8	1.7	–	–	–	–	2.0	–
19. 2,6-Dimethylphenol (*2,6-Xylenol*)	1281	–	–	0.5	–	0.3	–	–	–
20. (*E*,*E*)-2,4-Decadienal	1291	8.7	2.0	–	–	–	0.1	5.1	3.8
21. (*E*)-2-Undecenal	1334	2.8	–	–	–	–	–	1.0	1.6
22. 2,5-Dihydrothiophene[b]	1368	–	0.2	–	0.1	–	–	–	0.2
23. Ethyl decanoate	1378	0.5	–	–	–	–	–	–	–
24. 2,6-Dimethoxyphenol	1383	0.6	–	–	1.2	–	0.1	–	0.2
25. 2,6-Di(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	1423	–	–	–	–	–	–	0.1	–
26. Decanoic acid (*Capric acid*)	1444	2.8	1.0	–	0.8	0.1	0.9	1.0	0.6
27. 2,6-Di(*tert*-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadiene	1462	1.3	–	–	0.3	–	0.1	0.2	0.3
28. Benzeneacetic acid	1469	–	0.1	–	–	–	0.4	–	0.2
29. Butyl hydroxytoluene (*BHT*)	1478	6.4	3.9	–	2.1	0.1	2.0	0.3	0.9
30. 4-Hydroxy-3-methoxy-benzaldehyde	1495	–	–	–	0.4	–	–	–	0.2
31. Pentadecane	1500	–	–	0.2	0.7	–	–	0.6	0.2
32. Dodecanoic acid (*Lauric acid*)	1619	0.9	0.5	–	–	0.5	0.8	1.3	0.7
33. 8-Heptadecene[b]	1648	–	–	–	–	–	–	–	0.2
34. 2-Pentadecanone	1657	1.5	–	0.2	–	0.2	–	0.5	–
35. Ethyl tetradecanoate	1776	0.5	–	–	–	–	–	–	–
36. Hexadecanal	1781	7.3	–	7.9	6.4	6.1	6.9	10.9	6.3
37. Tetradecanoic acid (*Myristic acid*)	1816	6.1	2.2	1.8	2.1	4.7	4.4	2.0	2.0
38. 1-Octadecene[b]	1850	–	–	–	–	–	–	0.4	–
39. 13-Octadecenal[b]	1874	–	–	0.5	0.4	0.4	0.1	0.7	0.3
40. 1,2-Dibutylbenzenedicarboxylate (*Dibutyl phthalate*)	1911	–	0.2	0.2	0.4	0.2	0.4	0.2	0.5
41. (*Z*)-9-Octadecenal	1946	–	–	3.5	1.5	2.1	1.6	5.1	1.2
42. Ethyl hexadecanoate	1972	0.4	–	–	–	–	–	–	–
43. Octadecanal	1974	–	–	3.3	1.9	2.9	2.2	4.5	1.8
44. Hexadecanoic acid (*Palmitic acid*)	2035	11.7	21.6	33.0	24.5	39.7	32.0	24.3	29.2
45. (*Z*)-9-Octedecenoic acid (*Oleic acid*)	2180	11.9	39.5	33.5	43.4	31.9	41.8	26.9	35.3
46. Octadecanoic acid (*Stearic acid*)	/	2.3	6.2	5.2	4.2	4.1	3.0	4.4	4.5
Total identified (%)		87.2	86.2	93.7	97.5	95.2	98.3	94.6	95.1
Yield (mg/kg)		41.5	330.2	74.4	278.8	56.9	323.7	65.2	215.3

RI – retention indices on HP-101 column; / – RI not calculated; sample A – smoked ham dry-cured for 60 days; sample B – smoked ham dry-cured for 365 days, sample C – smoked ham dry-cured for 910 days; sample D – fried smoked ham dry-cured for 365 days; – non-detected.

[a] Average of duplicate analysis of three batches of each sample by GC and GC–MS.

[b] Tentatively identified.

Table 2
Volatile compounds isolated by nitrogen purge and steam distillation (NPSD) from samples A–D

No. compound	RI (HP-101)	Percentage[a] (%)											
		First trap				Second trap				Third trap			
		D	C	B	A	D	C	B	A	D	C	B	A
1. 1,3-Dimethylbenzene	844	–	–	–	–	–	–	–	–	1.0	–	–	–
2. Heptanal	867	–	–	–	–	1.3	–	–	–	–	–	–	–
3. 2,5-Dihydrofuran	869	–	–	–	–	–	1.3	0.8	–	–	–	–	–
4. 2,5-Dimethylpyrazine	881	3.5	0.4	1.1	1.6	–	–	–	–	–	–	–	–
5. Furfuryl alcohol	920	2.9	2.1	4.9	6.5	–	–	–	–	–	–	–	–
6. Benzaldehyde	955	1.1	–	–	–	1.2	–	–	–	2.7	–	–	–
7. 2-Pentylfuran	966	–	–	–	–	–	4.0	–	–	3.8	–	–	–
8. 2-Ethyl-3-methylpyrazine	976	4.3	0.8	0.7	1.0	–	–	–	–	–	–	–	–
9. Octanal	978	–	–	–	–	3.5	–	1.6	–	–	–	–	–
10. Decane	1000	–	–	–	2.3	–	–	–	–	–	–	–	–
11. Phenylacetaldehyde	1025	3.4	4.0	4.6	2.6	1.7	–	2.0	–	–	–	–	–
12. 2-Methylbenzaldehyde	1041	–	–	–	–	–	2.6	–	–	–	–	–	–
13. Naphtalene	1179	–	–	–	–	–	6.0	–	–	–	–	–	–
14. Ethyl octanoate	1180	–	–	–	–	–	–	0.9	–	–	–	–	–
15. 2-Ethyl-1-hexanol	1034	–	–	–	–	–	–	–	–	–	–	–	4.1
16. 3,6-Dimethyldecane	1048	–	–	–	–	–	–	–	4.8	–	–	–	–
17. 2,5-Dimethyl-3-ethylpyrazine	1070	1.1	–	–	–	–	–	–	–	–	–	–	–
18. Nonanal	1072	–	–	–	2.3	6.3	12.7	5.7	2.1	–	–	–	4.4
19. Benzyl alcohol	1092	0.4	–	–	1.7	–	–	–	–	–	–	–	–
20. Undecane	1100	–	–	–	–	–	–	–	2.3	–	–	–	4.1
21. 2-Metoxyphenol (*Guaiacol*)	1116	3.5	2.6	6.5	5.0	–	1.4	0.6	–	–	–	–	–
22. Phenol	1137	3.2	7.0	3.8	7.5	–	–	–	–	–	–	–	–
23. Benzyl acetate	1152	–	–	–	–	–	–	–	0.5	–	–	–	11.8
24. 2-Phenylethanol	1159	–	–	–	1.1	–	–	–	–	–	–	–	0.6
25. 2-Methylphenol (*o-Cresol*)	1166	6.3	5.0	4.3	3.7	–	–	–	–	–	–	–	–
26. Decanal (*Capric aldehyde*)	1187	2.1	–	–	–	3.1	–	2.7	–	–	–	–	–
27. Dodecane	1200	–	–	–	–	–	–	–	–	1.0	–	–	4.0
28. 3-Methylphenol (*m-Cresol*)	1205	6.9	12.1	7.9	7.2	–	–	–	–	–	–	–	–
29. Benzothiazole	1226	–	–	–	0.3	–	–	–	–	–	–	–	5.7
30. (*E*)-2-Decenal	1232	–	–	–	–	–	–	–	1.1	–	–	–	–
31. 2,5-Dimethylphenol (*2,5-Xylenol*)	1246	1.6	4.5	2.5	2.4	–	–	–	–	–	–	–	–
32. 2,6-Dimethoxytoluene	1253	–	0.5	–	–	–	–	–	–	–	–	–	–
33. (*E,Z*)-2,4-Decadienal	1268	–	–	–	–	2.3	3.6	–	1.2	–	–	–	–
34. 4,6-Dimethylundecane	1274	–	–	–	3.1	–	–	–	–	–	–	–	–
35. 2,6-Dimethylphenol (*2,6-Xylenol*)	1281	0.2	13.3	5.8	0.7	–	1.3	–	–	–	–	–	–
36. *trans*-Anethole	1282	0.9	1.8	–	–	2.9	–	1.1	–	1.5	–	–	–
37. 1-Methylnaphtalene	1289	–	–	–	–	–	3.1	–	–	–	–	–	–
38. 4-Ethyl-2-methoxyphenol	1290	–	–	–	5.0	–	–	–	–	–	–	–	–
39. (*E,E*)-2,4-Decadienal	1291	–	–	–	2.1	–	3.6	–	4.5	–	–	–	–
40. Tridecane	1300	–	–	–	1.6	1.0	2.0	1.1	5.4	1.7	–	0.7	–
41. 4,6-Dimethyldodecane	1317	–	–	–	2.1	–	–	–	–	–	–	–	–
42. 4-Vinyl-2-methoxyphenol	1344	–	–	–	0.4	–	–	–	–	–	–	–	–
43. Dihydro-5-pentyl-2(3H)furanone[b]	1354	0.6	–	–	0.5	–	–	–	–	–	–	–	–
44. 2,4,6-Trimethylphenol	1364	–	–	–	0.4	–	–	–	–	–	–	–	–

45. 2,5-Diethylphenol	1367	1.2	–	–	–	–	–	–	–	–	–	–	–
46. 1,4-Di(1,1-dimethylethyl)-benzene	1370	–	–	–	–	–	–	–	–	–	–	–	4.9
47. 4-Propyl-2-methoxyphenol	1374	–	–	–	0.8	–	–	–	–	–	–	–	–
48. Ethyl decanoate	1378	–	–	–	–	2.9	1.8	6.5	–	–	–	–	–
49. 2,6-Dimethoxyphenol	1383	3.2	14.4	1.8	1.4	–	0.7	–	–	–	–	–	–
50. 1,6-Dimethylnaphtalene	1412	–	–	–	–	–	1.0	–	–	–	–	–	–
51. Tetradecane	1400	–	–	–	–	5.1	–	7.6	–	1.8	–	–	5.6
52. Decanoic acid (*Capric acid*)	1444	2.1	–	–	0.4	–	–	–	–	–	–	–	–
53. Biphenylene	1449	–	–	–	–	–	1.3	–	–	–	–	–	–
54. Butyl hydroxytoluene (*BHT*)	1478	4.5	4.8	1.3	6.3	28.0	7.5	4.5	18.9	19.3	6.0	7.4	13.6
55. Pentadecane	1500	–	–	–	–	1.4	–	–	10.1	0.8	–	1.3	–
56. Dibenzofuran	1515	–	–	–	–	–	1.8	–	–	–	–	–	–
57. Ethyl dodecanoate	1579	1.0	–	1.4	–	1.0	–	2.5	–	–	–	–	–
58. Hexadecane	1600	–	–	–	0.4	1.6	1.1	3.0	–	–	–	–	2.6
59. Dodecanoic acid (*Lauric acid*)	1619	3.7	1.1	2.7	0.7	–	–	–	–	–	–	–	7.3
60. 2-Pentadecanone	1657	1.6	–	–	0.6	–	–	–	–	–	–	–	–
61. Heptadecane	1700	–	–	–	2.4	–	–	–	10.1	–	–	–	3.6
62. 1-Ethyldibenzothiophene	1701	0.7	–	–	–	1.4	–	–	–	–	–	–	–
63. 3,4-Diethyl-1,1′-biphenyl	1732	–	–	–	–	–	–	2.7	–	–	–	–	–
64. Ethyl tetradecanoate	1776	0.7	–	1.1	–	–	–	–	–	–	–	–	–
65. Hexadecanal	1781	4.3	–	16.7	10.8	–	–	–	1.5	–	–	–	–
66. Octadecane	1800	–	–	–	–	–	–	–	0.7	2.3	15.9	2.0	2.5
67. Tetradecanoic acid (*Myristic acid*)	1816	–	–	–	0.3	–	2.4	–	–	–	–	–	–
68. 1,2-(2-Methylpropyl)-benzenedicarboxylate	1848	1.6	–	4.4	–	0.8	–	4.9	–	–	–	–	–
69. 1-Octadecene[b]	1850	–	0.9	–	–	–	–	–	–	–	–	–	–
70. Nonadecane	1900	–	–	–	–	–	–	–	4.0	3.8	–	2.8	–
71. 1,2-Dibuthylbenzenedicarboxylate (*Dibutyl phthalate*)	1911	5.1	2.6	4.6	0.2	–	2.4	9.2	–	–	–	–	–
72. 2-Methyloctadecane	1941	–	–	–	–	–	–	–	2.5	–	–	–	–
73. (*Z*)-9-Octadecenal	1946	–	–	–	0.4	–	–	–	–	–	–	–	–
74. Ethyl hexadecanoate	1972	1.3	–	4.1	–	–	–	–	–	–	–	–	–
75. Eicosane	2000	–	0.2	–	–	2.1	2.0	12.8	–	3.2	–	29.1	–
76. Hexadecanoic acid (*Palmitic acid*)	2035	7.1	5.0	7.6	0.6	–	3.1	2.6	–	–	5.0	–	1.6
77. Heneicosane	2100	1.7	–	–	–	2.4	4.4	–	0.8	10.8	8.4	–	–
78. (*Z*)-9-Octadecenoic acid (*Oleic acid*)	2180	–	1.4	–	0.9	–	–	–	–	–	–	–	2.5
79. Docosane	2200	–	–	–	–	–	–	–	–	15.2	–	–	–
80. Tricosane	/	–	–	–	–	5.8	5.5	–	–	2.7	36.0	36.9	–
81. Pentacosane	/	–	–	–	–	–	7.0	–	–	2.5	7.0	–	–
Total identified (%)		81.8	84.5	87.8	87.3	75.9	83.6	72.8	70.5	74.1	78.3	80.2	78.9
Yield (mg/kg)		4.0	12.0	10.2	2.4	3.1	3.4	2.0	1.8	0.5	0.2	0.4	0.2

RI – retention indices on HP-101 column; / – RI not calculated; sample A – smoked ham dry-cured for 60 days; sample B – smoked ham dry-cured for 365 days, sample C – smoked ham dry-cured for 910 days; sample D – fried smoked ham dry-cured for 365 days; – non-detected.

[a] Average of duplicate analysis of three batches of each sample by GC and GC–MS.

[b] Tentatively identified.

Nitrogen purge and steam distillation (NPSD) was used to isolate the headspace volatiles (samples A–D) into three different fractions depending on their volatility and solubility, with little or no interference from medium volatile constituents that were present in high concentration in the SE and SDE isolates. Once these interferences were eliminated, analysis of the minor but important flavour components, such as phenols, lower aldehydes and heterocyclic compounds, became easier. Although NPSD was done at 102 ± 5 °C this is not the standard cooking process, since nitrogen not only serves as a carrier gas, but also provides an inert medium which prevents oxidation of unsaturated fatty acids, sugars and amino acids (Ai-Nong & Bao-Guo, 2005; Ramarathnam et al., 1993). The first cold trap mainly served to condense the water vapour and collect the water-soluble components and yielded 2.4–12 mg kg^{-1} that constituted 54.4–76.9% of all the NPSD identified volatiles. Fifty-one compounds were identified in the first trap (Table 2) including aldehydes, carboxylic acids, alcohols, ketones, esters, phenols, heterocyclic compounds and fatty acids. The percentage of fatty acids is markedly less in comparison with the SDE and SE extracts due to their lower volatility and consequently lower headspace concentration. The second cold trap containing 50 mL ether is mainly used for trapping the more volatile compounds that are not condensed earlier in the first trap. The mass concentration of identified compounds amounted to 1.8 mg kg^{-1} up to 3.4 mg kg^{-1} and was generally lower than that in the first cold trap. Forty-seven compounds were identified in this second trap (Table 2), mainly being aldehydes, esters and hydrocarbons. The third cold trap, containing 50 mL of *n*-pentane is mainly used for trapping the compounds that escaped absorption in the first and second cold traps. The yield of this fraction was the lowest in all the traps and amounted to 0.2 mg kg^{-1} up to 0.5 mg kg^{-1}. In all, 28 compounds were identified in this trap (Table 2), and they where mainly hydrocarbons.

3.1. Samples from the different curing periods

3.1.1. Volatiles isolated by SE and SDE methods

The isolated volatile flavour compounds of Dalmatian smoked and dry-cured ham by the SE and SDE methods (samples A–C, Table 1) could be classified into the following several chemical groups: saturated and unsaturated acids, aldehydes, ketones, phenols and aromatic compounds. The volatile components with the highest area percentage in all chromatograms were hexadecanoic acid (11.7–39.7%) and (*Z*)-9-octadecenoic acid (11.9–43.4%). The high percentage of these acids found in the isolates (A–C) obtained by both methods was expected given the large amount of fat in the samples. However, their proportions varied strongly between the SE and SDE extraction techniques (Table 1) for all samples, and the content of (*Z*)-9-octadecenoic acid was always higher in the SE extracts. Lipids show intensive lipolysis during dry-curing, especially during salting and post-salting, while the free fatty acids accumulate as a result of triglycerides hydrolysis (Moltiva, Toldrà, Nieto, & Flores, 1993). Due to their low volatility, their contribution to ham flavour might be of less importance (Dirinck et al., 1997). Other straight-chain carboxylic acids such as 3-butenoic acid (0.0–0.9%), butanoic (0.0–0.6%), pentanoic (0.0–0.4%), hexanoic (0.0–0.9%), octanoic (0.0–0.5%), decanoic (0.0–2.8%), dodecanoic (0.0–0.9%), tetradecanoic (1.8–6.1%) and octadecanoic acid (2.3–6.2%) were also present, Table 1. Linear saturated aldehydes (nonanal (0.0–1.5%), hexadecanal (6.1–7.9%) and octadecenal (0.0–3.3%)), as well as linear unsaturated aldehydes (such as (*E*)-2-heptenal (0.0–0.2%), (*E*)-2-decenal (0.0–4.9%), (*E*,*Z*)- and (*E*,*E*)-2,4-decadienal (0.0–8.7%), (*E*)-2-undecenal (0.0–2.8%), 13-octadecenal (0.0–0.5%) and (*Z*)-9-octadecenal (0.0–3.5%)) were also identified, Table 1. From a biochemical point of view, linear saturated (C_5 to C_{10}), unsaturated (C_6 to C_{11}) and polyunsaturated aldehydes with more than five C-atoms originate from lipolysis auto-oxidation mechanisms (Belitz & Grosch, 1987). These compounds have distinctive odour characteristics (especially low-molecular-weight ones) and low threshold values and, in general, contribute to the ham flavour. 2-Pentadecanone (0.2–1.5%) was identified (SDE) as the only methylketone, Table 1. According to Hinrichsen and Pedersen (1995), ethyl esters are formed enzymatically in the final stage of ripening by combining alcohol and acids, and three ethyl esters were identified in sample C (Table 1): ethyl decanoate (0.0–0.5%) ethyl tetradecanoate (0.0–0.5%) and ethyl hexadecanoate (0.0–0.4%). No low molecular weight esters were detected. Smoked meat flavour is mainly due to the phenols present in the wood smoke (Hanson, 2000), although Hanson did not report the specific phenols. In this study (SE and SDE), seven phenols were identified: guaiacol (0.0–0.9%), phenol (0.1–2.6%), *o*-cresol (0.0–0.6%), *m*-cresol (0.0–2.4%), 2,5-xylenol (0.0–0.2%), 2,6-xylenol (0.0–0.5%) and 2,6-dimethoxyphenol (0.0–1.2%). Methoxyphenols are components of great importance for smoke flavour and for their preserving and antioxidant effect. The smoke methoxyphenols reflect the structure of the corresponding units in the wood lignin. One heterocyclic compound (2-pentylfurane) that originated from the Maillard reaction (which is known to occur in heated, dried, or stored foods and *in vivo* in mammalian organisms (Fay & Brevard, 2005)) was identified in Table 1.

Regarding the impact of the dry curing period on the volatile flavour compounds, an increase in the percentages of carbonyls during the ripening of the ham was observed (Table 1). These differences were especially pronounced for aldehydes, such as phenylacetaldehyde, nonanal, (*E*)-2-decenal, (*E*)-2-undecenal and hexadecanal. These results are in agreement with the reports on the ripening of Iberian ham where after 420 days higher levels of compounds derived from lipid oxidation were found (Ruiz et al., 1999). The percentage of butanoic, decanoic and dodecanoic acids was also higher in sample C (Table 1), as well as the amount of ethyl decanoate. The amount of 2-pentylfuran was also the highest in sample C (1.3%) with the longest

curing period (910 days), Table 1. 2-Pentylfurane is a non-carbonyl oxidation product from linoleic and other *n*-6 fatty acids, frequently found in dry-cured ham and it shows a relatively low threshold with a vegetable aromatic note (Fay & Brevard, 2005). The percentage of furfuryl alcohol was the highest in samples C and B (0.1–0.6%), while it was not present in sample A, Table 1. An increase of the percentage of smoke derived phenols (guaiacol, phenol, *o*- and *m*-cresol) in samples B and C was also observed (Table 1), probably due to their inside diffusion to the ham surface.

3.1.2. Volatiles isolated by NPSD method

Flavour important constituents of the first cold trap for samples A–C (Table 2) were phenols such as guaiacol (2.6–6.5%), phenol (3.8–7.5%), *o*-cresol (3.7–5.0%), *m*-cresol (7.2–12.1%), 2,5-xylenol (2.4–4.5%), 2,6-xylenol (0.7–13.3%), 4-ethyl-2-methoxyphenol (0.0–5.0%), 4-vinyl-2-methoxyphenol (0.0–0.4%), 2,4,6-trimethylphenol (0.0–0.4%), 2,6-dimethoxyphenol (1.4–14.4%), 4-propyl-2-methoxyphenol (0.0–0.8%) and 2,6-dimethoxyphenol (1.4–14.4%). The NPSD method revealed five more phenols in comparison with the SDE and SE methods. Other isolated and odour important components (Table 2) were carbonyls phenylacetaldehyde (2.6–4.6%), nonanal (0.0–2.3%), (*E*,*E*)-2,4-decadienal (0.0–2.1%), 2-pentadecanone (0.0–0.6%), hexadecanal (0.0–16.7%) and (*Z*)-9-octadecenal (0.0–0.4%). Decanoic acid (0.0–0.4%), dodecanoic acid (0.7–2.7%), tetradecanoic acid (0.0–0.3%), hexadecanoic acid (0.6–7.6%) and (*Z*)-9-octadecenoic acid (0.0–1.4%) were also isolated. Furfuryl alcohol (2.1–6.5%), 2,5-dimethylpyrazine (0.4–1.6%) and 2-ethyl-3-methylpyrazine (0.7–1.0%) were only identified in the first trap (Table 2), while pyrazines were not identified by SDE and SE (Table 1). Among the major components of the second trap (Table 2), the percentage changes (samples A–C) were: aldehydes octanal (0.0–1.6%), nonanal (2.1–12.7%), decanal (0.0–2.7%), (*E*)-2-decenal (0.0–1.1%) and (*E*,*Z*)-2,4-decadienal (0.0–3.6%); hydrocarbons 3,6-dimethyldecane (0.0–4.8%), undecane (0.0–2.3%), 1-methylnaphtalene (0.0–3.1%), tridecane (1.1–5.4%), tetradecane (0.0–7.6%), butyl hydroxytoluene (4.5–18.9%), pentadecane (0.0–10.1%), hexadecane (0.0–3.0%), heptadecane (0.0–10.1%), nonadecane (0.0–4.0%), eicosane (0.0–12.8%), heneicosane (0.0–4.4%), tricosane (0.0–5.5%) and pentacosane (0.0–7.0%); and esters ethyl octanoate (0.0–0.9%) ethyl decanoate (0.0–6.5%) and ethyl dodecanoate (0.0–2.5%). The major compounds isolated in the third trap (Table 2) varied among samples A–C as follows: butyl hydroxytoluene (7.4–13.6%) benzyl acetate (0.0–11.8%), dodecanoic acid (0.0–7.3%), tetradecane (0.0–5.6%), heneicosane (0.0–8.4%) tricosane (0.0–36.9%) and pentacosane (0.0–7.0%).

Regarding the general trend of volatiles isolated by the NPSD method, with respect to the dry curing period of the ham, an increase in the percentages of esters (ethyl decanoate, ethyl dodecanoate, ethyl tetradecanoate and ethyl hexadecanoate) and some lower aldehydes (nonanal, octanal, decanal) during the ripening of the ham was observed (Table 2). Using the NPSD method, more esters and carbonyls compared to the SE and SDE methods (Table 1) were identified – these could be important for detecting the final stage of the ripening process (Hinrichsen & Pedersen, 1995). The concentrations of 2-pentylfuran and 2,5-dihydrofuran were also the highest in sample C (Table 2) that had the longest curing period (910 days). An increase in the percentage of some phenols (2,6- and 2,5-xylenol, *o*- and *m*-cresol 2,6-dimethoxyphenol) in samples B and C (Table 2) was also observed. The percentages of 2,5-dimethylpyrazine and 3-methylpyrazine decreased with ripening.

3.2. Fried samples

Volatiles from fried prosciutto (sample D) were isolated by SDE (with the yield 65.2 mg kg^{-1}) and by SE (with the yield 215.3 mg kg^{-1}), Table 1. Based on the relative percentages (Table 1), the majority of fried prosciutto aroma compounds were lipid-derived and only a few originated from sugar degradation and/or Maillard reactions. It was observed that fried samples contained essentially the same components as non-fried samples, but with different proportions. Only one furan (2-pentylfuran that can also originate by degradation of 2,4-decadienals) was present and it has already been described as meaty (Ohloff & Flament, 1978). Another contributor to the fried aroma was phenylacetaldehyde, the Strecker aldehyde of phenylalanine (Whitfield, 1992). Quantitative percentage differences among fried and raw samples were particularly evident in respect of the aldehydes. The most abundant aldehydes identified in the fried sample D (Table 1) were (SDE; SE): nonanal (0.3%, 0.2%), (*E*)-2-decenal (1.2%, 3.1%), (*E*,*Z*)-2,4-decadienal (2.0%, 0.0%), (*E*,*E*)-2,4-decadienal (5.1%, 3.8%), (*E*)-2-undecenal (1.0%, 1.6%), hexadecanal (10.9%, 6.3%), 13-octadecenal (0.7%, 0.3%), (*Z*)-9-octadecenal (5.1%, 1.2%) and octadecanal (4.5%, 1.8%), whereas the raw samples contained lower levels of these aldehydes. The identified nonanal is formed from oleic acid, whilst hexanal (a typical oxidation product of linoleic acid) was not identified, probably due to its lower volatility. Oxidation products of linoleic acid, such as (*E*,*E*)-2,4-decadienal, were also found. The higher content (SDE, Table 1) of decanoic acid (1.0%), dodecanoic acid (1.3%) and tetradecanoic acid (2.0%) could be explained by further oxidation of the corresponding aldehydes.

The NPSD method enabled scrutiny of the volatiles (especially for compounds of lower molecular weight) from fried sample D (Table 2) without any interference of the heavier components. In the first trap, a percentage increase of the flavour important pyrazines (2,5-dimethylpyrazine (3.5%), 2-ethyl-3-methylpyrazine (4.3%) and 2,5-dimethyl-3-ethylpyrazine (1.1%)) were observed, while these compounds were not identified by SE and SDE (Table 1). Fried flavour in foods is usually associated with the presence of heterocyclic compounds such as pyrazines (Mottram, 1998), that are formed from the condensation of two

α-aminoketones (formed by Strecker degradation) by dicarbonyl compounds. Also, there was (Table 2) an increase in the percentage of decanal (2.1%), decanoic acid (2.1%), dodecanoic acid (3.7%) and 2-pentadecanone (1.6%) similar to that found by the SE and SDE methods (Table 1). In the second trap of fried sample D, there were remarkably higher percentages of the lower saturated aldehydes such as heptanal (1.3%), benzaldehyde (1.2%), octanal (3.5%) and decanal (3.1%) in comparison with the raw samples A–C, Table 2. Among these, only nonanal was identified in the SE and SDE extracts (Table 1). The third trap mainly contained hydrocarbons, as well as 2-pentylfuran (3.8%) and benzaldehyde (2.7%).

Qualitative and quantitative differences in the volatile patterns of fried and raw samples probably account for their different flavours. However, it is logical to assume that only a few components are responsible for the characteristic fried aroma, such as pyrazines and carbonyls (lower aldehydes and (*E*,*E*)-2,4-decadienal that contribute to the deep-fried note (Stier, 2000)). It must be taken into consideration that, even from simple frying model systems, many volatile compounds are formed which, at the frying temperature, are leaving the sample and thereby the causing the composition of the mixture to continuously change.

4. Conclusions

Most of the volatile compounds found in Dalmatian smoked and dry-cured ham come from lipolysis, proteolysis and lipid auto-oxidation, while 12 identified phenols are suggested to be generated during smoke curing. The profile of the isolated chemical families varied significantly with the extraction technique, and the NPSD method facilitated the identification of the flavour important headspace volatiles (phenols, lower aldehydes) with less or no interference from the medium volatile compounds present in high concentrations in the SDE and SE isolates. Using the NPSD method, more esters and carbonyls were identified than compared to the SE and SDE methods, an aspect that could be important for detecting the final stages of the ripening process. The NPSD method isolated low-molecular volatiles from fried ham, while the flavour important thermally derived pyrazines (2,5-dimethylpyrazine, 2-ethyl-3-methylpyrazine and 2,5-dimethyl-3-ethylpyrazine) and the most of lower aldehydes were not isolated by the SE and SDE methods.

There are differences in the volatile compound compositions among the six types of hams from the south European countries (Dirinck et al., 1997; Sabio et al., 1998) and Dalmatian prosciutto (depending on the type of raw material, processing technology and isolation methods used). The major difference seems to be the presence of phenols (guiacol, phenol, *o*- and *m*-cresol, 2,5- and 2,6-xylenol, 2,6-dimethoxyphenol) in all the isolates (SE, SDE and NPSD) from Dalmatian prosciutto that is probably responsible for the smoked flavour.

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