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Physicochemical properties and oxidative stability of liver pâté as affected by fat content

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Abstract

This study provides data on the physicochemical characteristics and oxidative stability of liver pâtés with different fat contents. Pâtés with high-fat contents (HFC) presented a smaller cooking yield than pâtés with medium and low fat contents (MFC and LFC, respectively) ($p < 0.05$), mainly due to a higher loss of lipids. Fat content was closely related to the calorific value of pâtés, these being more calorific in those with higher fat contents. Pâtés with LFC were darker (lower L^* value; $p < 0.05$), redder (higher a^* value; $p < 0.05$) and harder (higher hardness value; $p < 0.05$) than those with HFC. Oxidation stability of pâtés was affected by lipid content. HFC pâtés showed higher lipid and protein oxidation than LFC ones ($p < 0.05$), as measured by thiobarbituric acid-reactive substances and carbonyl content, respectively. Generation and release of lipid-derived volatiles might be affected by fat content because increases from 20% to 26% of fat in pâtés caused higher amounts of volatiles to be detected. A higher increase (from 26% to 31%) resulted in a decrease of total volatiles detected.

Keywords: Liver pâté; Fat content; Cooking yield; Instrumental colour; Texture; Lipid and protein oxidation

1. Introduction

Foodstuffs obtained from animals may be injurious to human health because of the high content of fat, the presence of large proportions of saturated fatty acids and cholesterol (Jiménez-Colmenero, Carballo, & Cofrades, 2001). In spite of that, meat and meat products are essential components of the human diet and provide, among other components, high quality protein, vitamins and large amounts of essential metals, such as iron. However, consumer concerns about the relationship between health and nutrition, challenge food technologists to develop new meat and fat-based products with improved characteristics. In order to answer the demand from consumers, many low-fat products have been developed in order to reduce the presence of lipids and several lipid oxidation products considered to be risks for human health, such as free-radicals, malondialdehyde (MDA) and cholesterol oxidation products (COPs) (Khegal, Prusa, & Hughes, 1987; Sylvia, Claus, Marrito, & Rigel, 1994; Troutt et al., 1992). On the other hand, the reduction of fat in meat products might affect their sensory characteristics (reviewed by Jiménez-Colmenero, 2000), mainly in those with a particularly high content of this component, such as patties, cooked sausages or liver pâté. Among several sensory traits, fat has been demonstrated to influence palatability and aroma characteristics of meat and fat products (Berry & Leddy, 1984; Chevance & Farmer, 1999; Jo, Lee, & Ahn, 1999; Troutt et al., 1992). The reduction of fat in foodstuffs is thought to modify their aromatic profile, since large amounts of volatiles are generated from lipid oxidation and their interaction with other food components (Mottram, 1998). Moreover, lipids influence physical and chemical stability of flavours because reduction of

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fat content will result in flavour losses due to an increase of aroma compound volatility (De Ross & Graf, 1995). The equilibrium between generation and release of volatile compounds from the food matrix might have a decisive impact on odour sensation since flavour is generally understood to be the perception of volatile compounds released from food while eating (Lubbers, Landy, & Voilley, 1998). Nevertheless, limited information is available on the release of volatile compounds from meat and fat products with different lipid contents.

Overall, the level of fat in foods is closely related to numerous quality traits and, in finely comminuted mixtures, such as liver pâté, the producer determines the fat content, and this decision may affect the nutritional, technological and sensory characteristics of the manufactured product (Jiménez-Colmenero, 2000). As far as we know, few studies concerning the physicochemical characteristics of pork liver pâté have been accomplished (Estévez, Morcuende, Ramirez, Ventanas, & Cava, in press; Rosmini et al., 1996) and the effect of different levels of fat on the physicochemical and oxidation stability characteristics of liver pâtés remains unknown. This investigation was undertaken to gain more information on the characteristics of pork liver pâtés and to study the effect of fat content on the physicochemical and nutritional characteristics and oxidation stability of this product.

2. Materials and methods

2.1. Animals, feed and sampling

Seven Iberian pigs, commonly produced in the South–West of Spain and belonging to Iberian pig pure breed selection schemes, were free-range-reared and fed on natural resources (grass and acorns), following the traditional livestock farming for Iberian pigs. The animals were slaughtered at ~150 kg live weight and an age of 12 months. After slaughter, back fat, muscle *quadriceps femoris*, and liver were removed from carcasses which were vacuum-packaged and stored at −80 °C until the manufacture of the experimental pâtés.

2.2. Manufacture of the liver pâté

The experimental pâtés were manufactured in a pilot plant. The formulation of the experimental pâtés is presented in Table 1. For all pâtés, the sum of the contents of back fat and meat in their formulation represented 50% of the total of the ingredients. Depending on the content of back fat used for the manufacture of pâtés, three different formulations were considered: low, medium and high-fat content (LFC, MFC or HFC; $n = 5$ for each) with 35%, 40% and 45% of fat, respectively. LFC, MFC and HFC pâtés presented 5%, 10% and 15% of meat in their compositions, respectively. The range of fat contents was chosen, based on the diversity generally found in the Spanish market. The other ingredients were as follows per 100 g of elaborated product: 33 g liver, 11.5 g distilled water, 2 g milk powder, 2 g sodium chloride, 1 g caseinates. Sodium di- and tri-phosphates (0.5%), sodium ascorbate (0.025%) and sodium nitrite (0.05%) (ANVISA, Madrid, Spain), were also added. On the day of manufacture, the adipose tissue, livers and muscles from Iberian pigs were chopped into small cubes (1.5 cm^3). The livers and meat were mixed during mincing in a cutter (Foss Tecator Homogenizer, mod. 2094) during 3 min. During this period, water, in the form of small cubes of ice, was added to the bowl and mixed with the aforementioned ingredients in order to protect the batter from temperatures above 15 °C. After that, the other ingredients were added (small cubes of fat, the last ones in being added to the mixture in order to minimise possible oxidation during mincing). The whole mixture was completely minced during 6 min until a homogeneous raw batter was obtained. Finally, the mixture was packed in plastic containers and given the thermal treatment (85 °C/30′). The packed liver pâtés were kept frozen (−80 °C) until required for analytical experiments.

Table 1
Recipe (% of ingredients) used for liver pâtés with different fat contents

Ingredient (%)	LFC	MFC	HFC
Back fat	35	40	45
Liver	33	33	33
Muscle	15	10	5
Water	11.5	11.5	11.5
Milk powder	2	2	2
Salt	2	2	2
Caseinates	1	1	1
Phosphates	0.5	0.5	0.5
Sodium nitrite	0.05	0.05	0.05
Sodium ascorbate	0.025	0.025	0.025

2.3. Analytical methods

2.3.1. Cooking yield

Cooking yield was determined by assessing the value of exudation after thermal treatment. Each of the tubes was emptied on a sieve and drained. The exudative fluids (water and fat) were separated in order to measure fat and water losses. The processing yield was given by the mean value of the weight difference before and after thermal treatment for the tubes:

$$\%\text{Cooking yield} = \frac{\text{Drained pâté weight}}{\text{Batter weight}} \times 100.$$

2.3.2. Compositional analysis and calorific value of liver pâtés

Moisture, total protein and ash were determined using official methods (AOAC, 2000). The method of Bligh and Dyer (1959) was used for determining fat

content. Total iron was determined following the procedure described by Miller, Smith, Kanner, Miller, and Lawless (1994). Non-heme iron (NHI) content was determined following the method described by Rhee and Ziprin (1987). The amount of heme iron (HI) was calculated by difference between total and NHI. The content of carbohydrates was obtained by subtracting to the 100%, the contents of fat, protein, moisture and ash. The calorific value was calculated by taking into account the appropriate conversion factors for protein and carbohydrates (4 kcal/g) and fat (9 kcal/g).

2.3.3. pH measurement

The pH was determined using a Crison pH meter (mod. 2001) following the method of AOAC (2000).

2.3.4. Instrumental texture

The penetration test was performed with a Universal TA-XT2i texture analyser (Stable Micro Systems, UK). Force in compression was measured with a 10 mm diameter cylinder probe, using a 5 kg load cell. Once the probe triggered on the surface, it then proceeded to penetrate to a depth of 8 mm within the sample, measuring the force value as the hardness (N) of the sample. Force–distance deformation curves were recorded at a cross-head speed of 1.5 mm/s. Textural analyses were performed at ambient temperature.

2.3.5. Objective colour measurement

Instrumental colour (CIE L^* a^* b^*; CIE, 76) was measured in triplicate on the surface of liver pâtés using a Minolta Chromameter CR-300 (Minolta Camera Corp., Meter Division, Ramsey, NJ). Chroma (C) and Hue angle ($H°$) values were obtained by using the following equations: $C = (a^{*2} + b^{*2})^{0.5}$; $H° = \text{arctg}\ b^*/a^*$.

2.3.6. Lipid oxidation

MDA and other thiobarbituric acid-reactive substances (TBARS) were determined using the method described by Rosmini et al. (1996) for liver pâtés.

2.3.7. Protein oxidation

Protein oxidation, as measured by the total carbonyl content, was assessed following the method described by Oliver, Ahn, Moerman, Goldstein, and Stadtman (1987). Protein concentration was calculated by spectrophotometry, using BSA as standard.

2.3.8. Lipid-derived volatiles

The SPME fibre, coated with divinyl-benzene–carboxen–polydimethylxilosane (DVB/CAR/PDMS) 50/30 μm, was preconditioned prior analysis at 220 °C during 45 min. The headspace (HS) sampling was performed following a method previously described (Estévez, Morcuende, Ventanas, & Cava, 2003) with minor modifications as follows: 1 g of pâté was placed in a 2.5 ml vial and the SPME fibre was exposed to the HS of the pâté while the sample equilibrated during 30 min immersed in water at 60 °C. Analyses were performed on a HP5890GC series II gas chromatograph (Hewlett-Packard) coupled to a mass-selective detector. Volatiles were separated using a 5% phenyl–95% dimethyl polysiloxane column (30 m × 0.25 mm id., 1.0 mm film thickness; Restek). The carrier gas was helium at 18.5 psi, resulting in a flow of 1.6 ml min^{-1} at 40 °C. The SPME fibre was desorbed and maintained in the injection port at 220 °C during the whole chromatography run. The injector port was in the splitless mode. The temperature programme was isothermal for 10 min at 40 °C and then raised at the rate of 7 °C min^{-1} to 250 °C, and held for 5 min. n-Alkanes (Sigma R-8769) were run under the same conditions to calculate the Kovats index (KI) values for the compounds. The GC-MS transfer line temperature was 270 °C. The mass spectrometer operated in the electron impact mode with an electron energy of 70 eV, a multiplier voltage of 1650 V and collecting data at a rate of 1 scan s^{-1} over a range of m/z 40–300. Compounds were tentatively identified by comparing their mass spectra with those contained in the wiley/NIST/EPA/NIH libraries and by comparison of KI with those reviewed in the scientific literature.

2.4. Data analysis

In order to find differences between groups, results of the experiments were used as variables and analysed using an Analysis of Variance (ANOVA) from SPSS software (SPSS, 1997). The Tukey test was used to compare differences among mean values when ANOVA showed significance. Statistical significance was defined at 0.05. Principal component analysis (PCA), from SPSS software, was carried out to establish relationships between variables measured and to discriminate among groups of pâtés.

3. Results and discussion

3.1. Effect of fat content on cooking yield

Experimental pâtés suffered losses of lipids and water after the thermal treatment (Table 2). Cooking yield was improved in pâtés with lower fat contents from 86.74% (HFC) to 89.13% and 90.65% (LFC and MFC, respectively) ($p < 0.05$). These results are in good agreement with those previously reported on beef patties (Garzon et al., 2003; Troutt et al., 1992) and cooked sausages (Hughes, Mullen, & Troy, 1998; Pietrasik, 1999). Loss of water after cooking showed, no statistical differences among groups (LFC: 4.52 g water/100 g pâté; MFC: 4.25 g water/100 g pâté; HFC: 3.60 g water/100 g pâté) ($p > 0.05$). The differences in cooking yields among pâtés

Table 2
Cooking yield of pâtés and fluid losses (means ± standard deviation) after thermal treatment of raw batter from pâtés with different fat contents

	LFC	MFC	HFC	p^{A}
Cooking yield[B]	$88.13^{ab} \pm 4.43$	$89.65^{a} \pm 1.40$	$86.74^{b} \pm 9.85$	0.022
Water loss[C]	4.52 ± 2.30	4.25 ± 0.36	3.60 ± 1.49	0.553
Lipid loss[D]	8.56 ± 1.48	7.55 ± 1.30	11.42 ± 3.56	0.063

[a,b] Means in the same line with different superscript were statistically different.
[A] Statistical significance.
[B] Expressed as percentage.
[C] g water/100 g raw batter.
[D] g lipid/100 g raw batter.

were mainly caused by losses of fat after cooking since pâtés with the highest lipid content (HFC) lost 11.46 g fat/100 g pâté while MFC and LFC pâtés lost lower amounts of fat (7.55 and 8.56 g fat/100 g pâté, respectively; $p > 0.05$).

3.2. Effect of fat content on chemical composition and nutritional value of liver pâtés

As expected, the manufacture of liver pâtés with increasing fat contents resulted in products with different chemical compositions (Table 3). Parameters significantly affected by the fat content (moisture and total lipid content) showed an opposite behaviour. Moisture content followed the decreasing order: LFC > MFC > HFC ($p < 0.05$). In contrast, HFC pâtés had a higher lipid content (31.19 g/100 g pâté) than MFC (25.70 g/100 g pâté) or LFC (20.49 g/100 g pâté) ($p < 0.05$). Other parameters measured in the pâtés, such as protein (12.1–14.1 g/100 g pâté), carbohydrates (1.10–2.10 g/100 g pâté), ash (3.27–3.59 g/100 g pâté) and iron contents (73.9–80.6 mg/100 g pâté) did not show significantly differences among groups ($p > 0.05$). In spite of that, pâtés manufactured with lower fat content tended to present higher amounts of the aforementioned constituents, all of these being associated with the higher proportion of meat in the recipes. With reference to the chemical forms of iron, no differences between groups were found ($p > 0.05$) either for heme, nor for non-heme iron. Consequently, the role of heme and non-heme iron, in terms of bioavailability and promotion of lipid oxidation, seems to be similar in the samples studied. Mainly derived from the differences in the total lipid content, the pâtés presented significantly different caloric values, these being higher in those with high-fat content (HFC: 334 kcal/100 g pâté; MFC: 288 kcal/100 g pâté; LFC: 249 kcal/100 g pâté; $p < 0.05$). Liver pâté can be generally considered to be a high-caloric product with large amounts of fat (Jiménez-Colmenero, 2000; Mataix & Aranceta, 2002) and, therefore, its inclusion in the human diet might be restricted. However, previous considerations should be taken into account in order to consider the suitability of pâté for the human diet in relation to its fat content. The frequency of consumption of pâté is relatively low as long as it can be considered as a high quality product of fairly high price. Thus, the study of the quality of fat should the considered quantitatively and qualitatively, and therefore, the compositional characteristics of the fat may decide whether the pâté is a reasonably recommendable product or not. In the case of pâtés from Iberian pigs (as those manufactured for the present research), the large proportion of hypocholesterolemic fatty acids, such as oleic acid, reported in a previous work (Estévez et al., in press), make this product high-quality compared to pâtés from white pigs. Moreover, liver pâté is considered as one of the most important

Table 3
Chemical compositions and calorific values (means ± standard deviation) of liver pâtés from Iberian pigs with different fat contents

	LFC	MFC	HFC	p^{A}
Moisture[B]	$59.68^{a} \pm 1.18$	$56.98^{b} \pm 0.29$	$52.78^{c} \pm 1.49$	0.000
Fat[B]	$20.49^{c} \pm 1.22$	$25.70^{b} \pm 1.83$	$31.19^{a} \pm 1.38$	0.000
Protein[B]	14.1 ± .069	12.8 ± 2.07	12.1 ± 1.53	0.151
Carbohydrates[B]	2.10 ± 1.47	1.53 ± 1.13	1.10 ± 0.49	0.375
Ash[B]	3.59 ± 0.44	3.40 ± 0.39	3.27 ± 0.34	0.358
Total iron[C]	80.6 ± 9.23	78.1 ± 12.59	73.9 ± 6.64	0.469
Heme iron[C]	38.3 ± 10.66	32.3 ± 12.50	32.5 ± 9.48	0.531
Non-heme iron[C]	42.4 ± 6.87	45.8 ± 9.85	41.4 ± 7.33	0.572
Calorific value[D]	$249^{c} \pm 10.85$	$288^{b} \pm 2.39$	$334^{a} \pm 10.59$	0.000

[a,b,c] Means in the same line with different superscript were statistically different.
[A] Statistical significance.
[B] g/100 g pâté.
[C] μg/g pâté.
[D] kcal/100 g.

sources of high bioavailability iron and is therefore highly recommended in order to prevent iron deficiency. In low-fat pâtés the iron content could be enhanced by increasing the meat proportion in the recipe as long as the proportion of liver does not exceed 30% because of the intense taste of the product.

3.3. Effect of fat content on physical characteristics of liver pâté

Pâtés elaborated with different fat contents presented significant differences in most of the physical parameters assessed (Table 4). The pH values declined with increasing proportions of meat in the formulation of pâtés and followed the order: HFC > MFC > LFC. Fat content and hardness were inversely correlated (R^2: −0.70; $p < 0.01$) and, therefore, the presence of higher amounts of fat resulted in softer pâtés. HFC pâtés presented significantly lower values of hardness than LFC pâtés (0.95 N vs. 1.55 N, respectively, $p < 0.05$). The effect of fat on texture of meats and meat products has been extensively studied and it is generally assumed that larger contents of fat are related to less firm and more juicy products (Hughes et al., 1998; Sylvia et al., 1994; Troutt et al., 1992), agreeing with results obtained in the present work. The fat content significantly affected the instrumental colour displayed by pâtés. These results were expected because the colour of pâtés is closely related to the colour characteristics of the raw material used for the manufacture (Estévez et al., in press) and, therefore, changes in the proportion of the ingredients might lead to different colour characteristics. According to results from previous research on frankfurters and other meat products (Hughes et al., 1998; Troutt et al., 1992), the results in the present work, indicated that higher amounts of fat and lower of meat, increase lightness and reduce redness in the manufactured product. In fact, L^* was significantly ($p < 0.05$) correlated with fat content (R^2: 0.52). HFC pâtés were paler than LFC pâtés (L^* values: 54.20 vs. 51.74, respectively; $p < 0.05$), the latter being redder than the former (a^* values: 15.45 vs. 13.85). Consequently, LFC pâtés had a more intense colour (C values: 21.00 vs. 19.88) with lower values of hue ($H°$ values: 42.64 vs 45.83) when compared to pâtés with higher fat content.

Table 4
Instrumental texture and colour characteristics, pH and lipid (TBARS) and protein oxidation (carbonyls) (means ± standard deviation) of pâtés from Iberian pigs with different fat contents

	LFC	MFC	HFC	p[A]
Hardness[B]	$1.55^{a} \pm 0.26$	$1.29^{ab} \pm 0.36$	$0.95^{b} \pm 0.15$	0.016
pH	$6.34^{b} \pm 0.01$	$6.36^{b} \pm 0.01$	$6.39^{a} \pm 0.01$	0.000
Cie L^*	$51.74^{b} \pm 1.01$	$53.32^{ab} \pm 1.62$	$54.20^{a} \pm 1.19$	0.018
Cie a^*	$15.45^{a} \pm 0.09$	$14.74^{b} \pm 0.25$	$13.85^{c} \pm 0.31$	0.000
Cie b^*	14.21 ± 0.23	13.64 ± 0.89	14.25 ± 0.22	0.188
Chroma	$21.00^{a} \pm 0.19$	$20.09^{b} \pm 0.43$	$19.88^{b} \pm 1.96$	0.002
Hue	$42.64^{b} \pm 0.43$	$42.78^{b} \pm 1.96$	$45.83^{a} \pm 0.97$	0.003
TBARS[C]	$2.87^{b} \pm 0.40$	$3.76^{ab} \pm 1.24$	$5.56^{a} \pm 1.49$	0.018
Carbonyls[D]	$7.52^{b} \pm 30.1$	$8.54^{b} \pm 1.17$	$14.71^{a} \pm 3.63$	0.003

[a,b,c] Means in the same line with different superscript were statistically different.
[A] Statistical significance.
[B] Newtons.
[C] mg MDA/kg pâté.
[D] nmol carbonyls/mg protein.

3.4. Effect of fat content on oxidation stability of liver pâtés

The oxidation stability of liver pâtés, as measured by TBARS from lipid oxidation and carbonyls from protein oxidation, is shown in Fig. 1. The lipid content significantly affected lipid oxidation since HFC pâtés presented significant higher TBARS numbers, compared to pâtés with lower fat content (5.56 vs. 2.87 mg MDA/kg pâté; $p < 0.05$). These results were expected because TBARS are derived from lipid oxidation and, in similar circumstances, pâtés with higher fat content would present higher amounts of oxidation products. Working on different types of meat, Jo et al. (1999); Sasaki et al. (2001) and ourselves (Estévez, Morcuende, & Cava, 2003) found significant correlations between fat content and lipid oxidation, agreeing with results obtained in the present work (R^2: 0.52; $p < 0.05$).

Pâtés with higher MDA content presented, in addition, higher amounts of carbonyls from protein oxidation (Fig. 1). The carbonyl numbers were larger in pâtés with HFC (14.7 nmol carbonyls/mg protein) as compared to those with medium (8.54 nmol carbonyls/mg protein) and low-fat content (7.52 nmol carbonyls/mg protein) ($p < 0.05$). Reactive-oxygen species (ROS) and free-radicals from lipid oxidation are believed to attack and damage proteins, leading to a loss of functionality and formation of residues such as carbonyls (Stadtman, 1990). This fact would link both degradation phenomena and may explain the results obtained. In the

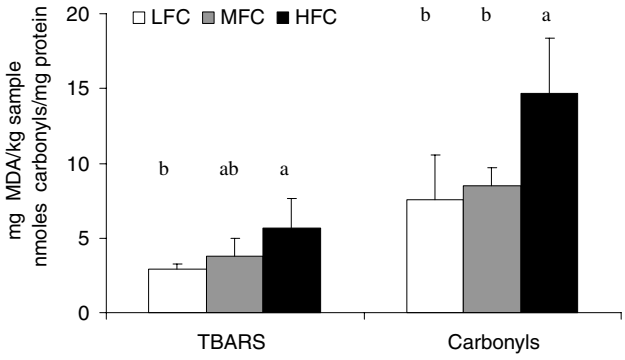

Fig. 1. Lipid and protein oxidation stability of liver pâtés with different fat content as assessed by TBARS (mg MDA/kg pâté) and carbonyls (nmol carbonyls/mg protein) content respectively (means ± SD). Different letters indicate significant differences between groups in a Turkey's 't' test.

present work, the loss of protein functionality probably had a reflection on the emulsion stability, as measured by cooking yield and fluid losses. Pâtés with higher oxidation instability (HFC ones) presented a lower cooking yield and higher losses of lipids after cooking. Thus, significant correlations were found between protein oxidation and cooking yield (R^2: −0.53; $p < 0.05$).

3.5. Effect of fat content on the generation and release of lipid-derived volatiles from liver pâtés

Nineteen lipid-derived volatiles were isolated from the HS of the experimental pâtés (Table 5). Taking into account the higher variability commonly found on the analysis of volatiles using SPME (Estévez et al., 2003) and the relatively small size of the groups in the present work ($n = 5$), it was unexpected to find large differences among groups. The level of fat in pâtés significantly affected the amount of major volatile compounds detected. Increasing the fat content, from 20% (LFC) to 26% (MFC), resulted in a significantly larger amount of lipid-derived aldehydes such as hexanal (LFC: 273 AU, MFC: 506 AU; $p < 0.05$), octanal (LFC: 17.6 AU; MFC: 27.9 AU; $p < 0.05$) and decanal (LFC: 1.8 AU; MFC: 3.6 AU; $p < 0.05$). The amounts of unsaturated aldehydes, such as non-(*E*)-2-enal (LFC: 5.5 AU, MFC: 15.3 AU; $p < 0.05$) dec-(*E*)-2-enal (LFC: 4.5 AU, MFC: 13.2 AU; $p < 0.05$), dodec-(*E*)-2-enal (LFC: 3.2 AU, MFC: 10.7 AU; $p < 0.05$) and 2,4 alkadienals, such as hepta-(*E*,*E*)-2,4-dienal (LFC: 3.1 AU, MFC: 10.8 AU; $p < 0.05$), nona-(*E*,*E*)-2,4-dienal (LFC: 3.9 AU, MFC: 18.0 AU; $p < 0.05$), deca-(*E*,*E*)-2,4-dienal (LFC: 4.5 AU, MFC: 7.9 AU; $p < 0.05$) and deca-(*E*,*Z*)-2,4-dienal (LFC: 3.3 AU, MFC: 10.7 AU; $p < 0.05$), were significantly higher in MFC pâtés than in LFC ones. Other lipid-derived volatiles, such as oct-1-en-3-ol (LFC: 13.1 AU, MFC: 30.1 AU; $p < 0.05$) and octan-2-one (LFC: 1.5 AU, MFC: 16.1 AU; $p < 0.05$) were in significantly larger amounts in MFC than in LFC pâtés. In clear contrast to the results described above, when comparing the volatiles profile from MFC pâtés (26% fat content) to that from HFC pâtés (~31% fat content), the amount of volatiles detected in the HS of liver pâtés, dramatically decreased. These differences are statistically significant for the most abundant compounds, such as hexanal (MFC: 506 AU, HFC: 318 AU; $p < 0.05$), octanal (MFC: 27.9 AU, HFC: 21.5 AU; $p < 0.05$), dodec-(*E*)-2-enal (MFC: 10.7 AU, HFC: 5.3 AU; $p < 0.05$), oct-1-en-3-ol (MFC: 30.1 AU, HFC: 15.0 AU; $p < 0.05$) and octan-2-one (MFC: 16.1 AU, HFC: 3.5 AU; $p < 0.05$). Higher amounts of other minority volatiles, such as heptan-2-one (MFC: 2.4 AU, HFC: 1.2 AU; $p < 0.05$) or 2-pentyl-furan (MFC: 5.5 AU, HFC: 2.8 AU; $p < 0.05$) were detected in MFC pâtés than in those with higher fat content. The results obtained in the present work suggest a contradictory effect of fat on the volatiles profile of liver pâtés. The increasing amount of total volatiles in MFC

Table 5
Lipid-derived volatiles (means ± standard deviation) from the headspace of liver pâtés from Iberian pigs with different fat contents as analysed using SPME

Volatile compounds	LFC	MFC	HFC	p^{A}
Butanal[B,C]	1.4 ± 0.2	3.4 ± 1.3	2.4 ± 1.8	0.091
Pentanal	7.8 ± 1.8	11.2 ± 4.5	8.6 ± 6.7	0.722
Hexanal	273^{b} ± 51.7	506^{a} ± 110	318^{b} ± 113	0.008
Heptanal	7.6 ± 0.5	11.3 ± 1.6	9.6 ± 4.9	0.203
Octanal	17.6 ± 4.4	27.9 ± 4.00	22.5 ± 9.8	0.084
Nonanal	55.5 ± 19.8	67.8 ± 11.3	57.1 ± 15.4	0.436
Decanal	1.8^{b} ± 0.5	3.6^{a} ± 0.8	3.1^{a} ± 1.1	0.009
Total saturated aldehydes	365^{b} ± 52.9	632^{a} ± 116	422^{b} ± 104	0.009
Hept-(*E*)-2-enal	9.6 ± 4.1	21.8 ± 10.3	12.9 ± 7.6	0.121
Hepta-(*E*,*E*)-2,4-dienal	3.1^{b} ± 1.7	10.8^{a} ± 3.6	7.8^{a} ± 1.7	0.001
Non-(*E*)-2-enal	5.5^{b} ± 3.1	15.3^{a} ± 4.5	10.5^{ab} ± 3.6	0.004
Nona-(*E*,*E*)-2,4-dienal	3.9^{b} ± 1.0	18.0^{a} ± 4.6	14.3^{a} ± 5.2	0.000
Dec-(*E*)-2-enal	4.5^{b} ± 2.6	13.2^{a} ± 1.2	10.4^{a} ± 4.2	0.001
Deca-(*E*,*E*)-2,4-dienal	4.5^{b} ± 1.5	7.9^{a} ± 1.8	5.4^{ab} ± 1.3	0.011
Deca-(*E*,*Z*)-2,4-dienal	3.3^{b} ± 2.2	10.7^{a} ± 1.5	9.1^{a} ± 2.9	0.000
Dodec-(*E*)-2-enal	3.2^{b} ± 1.7	10.7^{a} ± 3.4	5.3^{b} ± 0.8	0.000
Total unsaturated aldehydes	37.5^{b} ± 13.6	108^{a} ± 17.9	75.6^{ab} ± 15.2	0.001
Oct-1-en-3-ol	13.1^{b} ± 3.0	30.1^{a} ± 5.8	15.0^{b} ± 5.8	0.000
Heptan-2-one	1.5^{b} ± 0.7	2.4^{a} ± 0.5	1.2^{b} ± 0.2	0.004
Octan-2-one	1.5^{b} ± 0.5	16.1^{a} ± 5.1	3.5^{b} ± 1.3	0.007
2-pentil-furan	2.2^{b} ± 0.4	5.5^{a} ± 1.0	2.8^{b} ± 1.4	0.000
Total volatiles	420^{b} ± 53.0	794^{a} ± 154.6	520^{b} ± 129.3	0.002

[a,b] Means in the same line with different superscript were statistically different.
[A] Statistical significance.
[B] UAA/10^{6}.
[C] Volatile compounds tentatively identified using MS, KI and EPA/DHA/Nist and Wiley libraries.

compared to LFC pâtés was expected because these compounds are generated from lipid decomposition. As aforementioned for TBARS, foodstuffs with higher fat content, compared to those with lower fat content, are likely to present, under similar circumstances, larger amounts of lipid-derived products. If this fact were true, pâtés with the highest lipid content (HFC pâtés), in which the largest lipid and protein oxidation indices were found, might show the highest amount of lipid-derived volatiles. HFC pâtés are supposed to have generated larger amount of volatiles but they might not be detected with SPME if they were not present in the HS. These results are in good agreement with results from other authors (Ahn et al., 1998; Machiels & Istasse, 2002) and ourselves (Estévez et al., 2003, 2003) who reported higher amounts of lipid-derived volatiles in low-fat meat and meat products than in high-fat ones. In this sense, fat has been reported to reduce the release of volatiles from the food matrix to the HS (de Roos, 1997), avoiding their consequent detection by static or dynamic HS (Jo & Ahn, 1999; Chevance & Farmer, 1999). In agreement with aforementioned results, this suggests a clear dissimilarity between TBARS and lipid-derived volatiles for the measurement of lipid oxidation so that the former analysis provides accurate information despite the level of fat. In contrast to previous reports (Shahidi & Pegg, 1994), no significant correlations were found between the total amount of volatiles and TBARS (R^2: 0.06; $p > 0.05$). The level of fat in pâtés might affect the perception of the aroma as long as this sensation is related to the detection of volatile compounds released from the matrix of the food (Lubbers et al., 1998).

3.6. Principal component analysis

A principal component analysis (PCA) was carried out to determine the relationships between the parameters studied and to discriminate liver pâtés by their fat

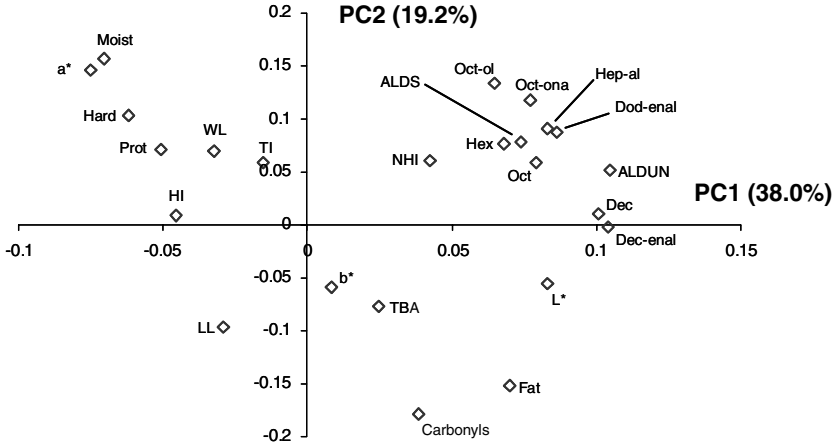

Fig. 2. Similarity map for the principal components (PC) 1 and 2 of the PC analysis performed on twenty-four physicochemical variables of liver pâtés with different fat content. Variables computed: Moisture (Moist), Fat content (Fat), Protein content (Prot), Total iron (TI), Non-heme iron (NHI), Heme iron (HI), Cie L^* (L^*), a^* (a^*), b^* (b^*), Hardness (Hard), Water (WL) and Lipid losses (LL), Protein oxidation (carbonyls), TBARS (TBA), Hexanal (Hex), Octanal (Oct), Decanal (Dec), Hept-(*E*)-2-enal (Hep-al), Deca-(*E*,*Z*)-2,4-dienal (Dec-enal), Doc-(*E*)-2-enal (Doc-enal), Octan-2-one (Oct-one) and Oct-3-en-1-ol (Oct-ol).

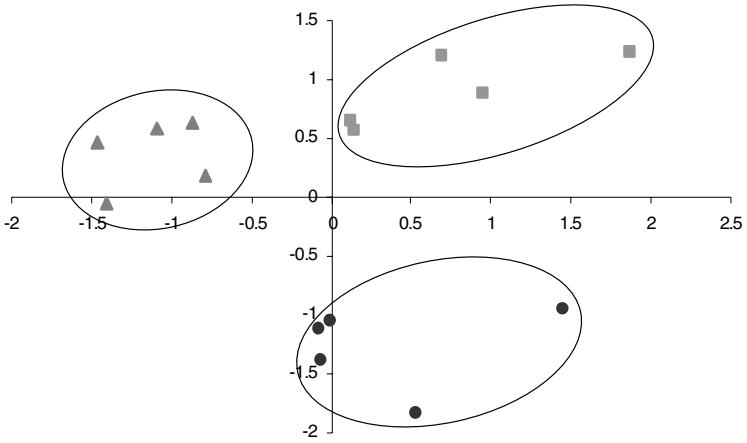

Fig. 3. Similarity map for the PC 1 and 2 of the PC analysis performed on the samples of pâtés elaborated with different fat content. Spots are grouped denoting the discrimination between formulations with low (▲) medium (■) or high-fat (●) content.

contents. Fig. 2 shows the similarity map defined by the two first principal components (PC#1 and PC#2, respectively) that accounted for 57.2% of the total variability. Agreeing with the aforementioned results, groups of variables were associated in the map, depending on the relationships established between them. Fig. 3 shows that the PC allowed us to clearly discriminate the three formulas of pâté with different fat contents. The pâtés with LFC are situated on the negative axis of PC#1, in the plane area corresponding to high values of moisture, protein, instrumental hardness and redness (Fig. 2). Pâtés with MFC, that showed the highest amount of lipid-derived volatiles, are grouped on the positive axis associated nearby high amounts of volatiles, such as hexanal, octanal, decanal, decan-(*E*,*Z*)-2,4-dienal, oct-3-en-1-ol and octan-2-one. Pâtés with HFC are mainly confined to the negative axis of the PC#2 and related to high oxidation numbers (from both protein and lipid oxidation), lightness and high lipid losses after thermal treatment.

4. Conclusion

Fat content affected the majority of physicochemical parameters measured. Some important quality traits, such as texture, appearance and nutritional value would show a clear relationship with the total amount of fat. Liver pâtés with higher fat content are more prone to suffer lipid and protein oxidation and produce less stable emulsions. Measurements of TBA-RS and carbonyls are appropriate methods to assess lipid and protein oxidation in liver pâtés while the information obtained from the lipid-derived volatiles analysis is not consistent to the ones obtained with the aforementioned methods, being the latter affected by fat content. Fat seems to be a source of lipid-derived volatiles but influences the release of these volatiles to the HS, preventing their detection using SPME at high levels of fat. The equilibrium between generation and release of volatile compounds in liver pâtés may influence the sensory perception of the aroma by consumers.

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