Changes on physico-chemical properties, lipid oxidation and volatile compounds during the manufacture of celta dry-cured loin

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Abstract The present study deals with the changes on the main technological characteristics and volatile compounds profile of a traditional Spanish dry-ripened loin from Celta pig breed. The evolution of physicochemical properties, colour, texture, free fatty acid profile and volatile compounds were assessed throughout the process seasoning, post-seasoning and after 30 and 60 days of dry-ripening.

As it was expected, pH, moisture and activity water were significantly ($P<0.001$) influenced by ripening time. Statistical analysis also displayed that colour parameters (lightness, L^* ; redness, a^* ; yellowness, b^*) decreased significantly ($P<0.001$) during the manufacturing process. On the other hand, lipid oxidation reached the highest levels at the end of process with mean values of 0.34 mg MDA/kg. Regarding total FFA, a significant ($P<0.001$) increase was observed during the manufacturing process, being MUFA the most abundant at the end of process. Finally, sixty seven volatile compounds were identified during the manufacture of Celta dry-cured loin. At the end of process, volatile compounds from microbial activity were the most abundant followed by volatile compounds from lipid oxidation.

Keywords Celta pig breed · Dry-cured loin · Free fatty acid · Physico-chemical properties · Volatile compounds

Introduction

Celta pig is a native breed of Galicia (NW Spain), classified as an autochthonous endangered breed (Spanish Regulation 2008), due to the introduction of improved breeds and their crosses. This breed is characterized by a great rusticity that allows a perfect ability to adapt to the conditions of the Galician forests, feeding on natural and seasonal resources (Carril et al. 2012). Celta dry-cured loin is one of the Celta meat products most appreciated by the consumers. The demand of Celta dry-cured meat products has grown recently, increasing from 623 animals in 2001 to 4882 at the end of 2012 (Carril et al. 2013).

The quality of dry-cured loin is based on both raw material composition and processing conditions (Muriel et al. 2004a). Meat quality parameters as colour, juiciness and hardness have provided results that support the conclusion that loin cut has very favorable characteristics for both fresh consumption and for the preparation of semi, elaborated and cured products. On the other hand, colour is the most important characteristic of appearance and textural parameters also contribute on the main attributes perceived by consumers (Ramírez and Cava 2007). This breed is highly appreciated by consumers because of the succulent meat that results from the profuse infiltration of fat into the lean meat (Franco et al. 2014) and the production of these pigs is mainly focused on the manufacture of dry-ripened meat products such as ham (Bermúdez et al. 2012, 2014a, 2014b), “lacón” (Garrido et al. 2012; Lorenzo et al. 2014; Purriños et al. 2011a, 2011b, 2012) and sausages (Gómez and Lorenzo 2013).

Processing has a great influence on the final flavor of dry-cured loins, with both seasoning/curing ingredients addition and the ripening/drying phases involving complex chemical and biochemical changes in the main components of the raw meat (proteins and lipids) leading to the generation of volatile compounds, which are mainly esters and sulphide compounds (Lorenzo 2014a; Muriel et al. 2004b). These compounds are

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responsible of the characteristic flavor of these products and they have influence on the consumer acceptance (Ruiz et al. 2002).

A considerable amount of studies have been devoted to describe processed loin quality at the end of ripening process, with respect to physicochemical characteristics and volatile profile. These researches were carried out with Iberian dry-cured loin (Muriel et al. 2004b; Ramírez and Cava 2007). However, there are not studies about dry-cured loin from Celta pig breed. Thus, the objective of this study was to assess the changes on physico-chemical properties, lipolysis and volatile compounds during the manufacture of Celta dry-cured loin.

Material and methods

Animal management

Twenty pigs from the Celta breed (Barcina line) were used. All specimens, registered in the Record of Births of Stud-Book were obtained from ASOPORCEL (Association of Celta pig breed). All animals were reared in a single group in an extensive system. They were fed *ad libitum* with commercial concentrate suited to the nutritive needs of the animals. Table 1 shows the chemical composition and fatty acid profile of the commercial feed. The day before slaughter, the animals were weighed and transported to the abattoir trying to minimize the stress of the animals. The animals were slaughtered at 12 months. Pigs were slaughtered in an accredited abattoir, using carbon dioxide to stun the animals (Lugo, Spain). Immediately after slaughter, carcasses were chilled at 4 °C in a cold chamber for 24 h. At this point, the *longissimus dorsi* muscle was excised from the right side of each carcass.

Manufacture of celta dry-cured loin

For this study, a total of twenty loins with an average weight of 1.70 ± 0.18 kg, were selected. Loins were seasoned by rubbing with 7.5 g per kg of supplement “Diana 655 AL” and 12 g per kg of supplement “Saboral Lomo Adobado B” from Cargill (Barcelona, Spain) composed, in unknown proportions, of sugar, salt, dextrin, olive oil, potassium nitrate (E₂₅₂), sodium nitrite (E₂₅₀), sodium ascorbate (E₃₀₁) and spices such as Spanish paprika (*Capsicum annuum*, L.), oregano (*Origanum vulgare*, L.) and garlic (*Allium sativum*, L.). Loins were kept at 4 °C for 3 days to allow the seasoning mixture to penetrate. Then, the loins were stuffed into collagen casings and transferred to a post-seasoning room where they stayed for 30 days at 2–5 °C and around 85–90 % relative humidity. After the post-seasoning stage, the pieces were transferred to a room at 12–14 °C and 74–78 % relative humidity where a drying-ripening process took place for 60 days. The air convection in

Table 1 Chemical composition and fatty acid profile of the commercial feed

Chemical composition	
Moisture (%)	10.68
Crude Protein (%)	13.34
Ash (%)	5.35
Fat (%)	5.55
Cellulose	4.1
Phosphate (%)	0.41
Ca (%)	1.04
Cu (mg/kg)	21
Fatty acid profile (%)	
C14:0	0.74
C16:0	19.69
C16:1n9	1.40
C17:0	0.21
C17:1	0.18
C18:0	6.10
C18:1n9c	36.94
C18:2n6c	30.85
C20:0	0.22
C20:1	0.92
C18:3n3	2.37
C20:2	0.28
C20:5n3	0.11
SFA	26.96
MUFA	39.44
PUFA	33.60
P/S	1.24
n-6/n-3	12.47

The concentrate was formulated using the following ingredients (%): 40 wheat, 25.5 barley, 15 soybean flour, 14.6 corn, 1.5 soybean oil, 2 calcium carbonate, 1 dicalcium phosphate and 0.20 sodium chloride

the drying room was intermittent and the air velocity around the pieces when the fan was running ranged between 0.3 and 0.6 m/s. Samples were taken after seasoning process, after post-seasoning stage and after 30 and 60 days of drying-ripening. In each sample point, five pieces were analyzed.

Analytical methods

pH, water activity, TBARs values and colour parameters

The pH of samples was measured using a digital pH-meter (Thermo Orion 710 A+, Cambridgeshire, UK) equipped with a penetration probe. Colour measurements were carried out using a CM-600d colorimeter (Minolta Chroma Meter Measuring Head, Osaka, Japan). Each loin was cut and the colour of the slices was measured three times for each analytical point. CIELAB space: lightness, (L*); redness, (a*); yellowness, (b*) were obtained. Before each series of measurements, the instrument was calibrated using a white ceramic tile. Lipid oxidation was assessed in triplicate by the 2-thiobarbituric acid (TBARs) method of Vyncke (1975) with

the modification that samples were incubated at 96 °C in a forced-air convection oven (Memmert UFP 600, Schwabach, Germany). Thiobarbituric acid reactive substances values were calculated from a standard curve performed with 1,1,3,3-tetraethoxypropane and expressed as mg malonaldehyde (MDA)/kg sample. Water activity was determined using a Fast-lab (Gbx, Romans sur Isère Cédex, France) water activity meter, previously calibrated with sodium chloride and potassium sulphate.

Chemical composition

Moisture, fat and protein (Kjeldahl $N \times 6.25$) were quantified according to the ISO recommended standards 1442:1997 (ISO 1997), 1443:1973 (ISO 1973) and 937:1978 (ISO 1978), respectively. Total chlorides were quantified according to the Carpentier-Vohlard official method ISO 184-1 (ISO 1996).

WB and Texture Analysis Profile

Seven meat pieces of 1×1×2.5 cm (height×width×length) were removed parallel to the muscle fibre direction and were completely cut using a Warner-Bratzler (WB) shear blade with a triangular slot cutting edge (1 mm of thickness). Maximum shear force, shear firmness and total necessary work performed to cut the sample were obtained. Texture profile analysis (TPA) was measured by compressing to 60 % with a compression probe of 19.85 cm² of surface contact. Force-time curves were recorded at a crosshead speed of 3.33 mm/s and recording speed was also 3.33 mm/s. Hardness (kg), cohesiveness, springiness (mm) and chewiness (kg×mm) were obtained. These parameters were obtained using the available computer software (Texture Exponent 32 version 1.0.0.68, Stable Micro Systems, Vienna Court, UK).

Free fatty acid

Total intramuscular lipids were extracted from 5 g of ground sample, according to Folch et al. (1957) procedure. Free fatty acids were separated from 20 mg of the extracted lipids using NH₂-aminopropyl mini-columns (Sep-Pak Vac 3 cc, 500 mg, Waters, Milford, MA) as described by Kaluzny et al. (1985). Free fatty acids were transesterified following the method described by Shehata et al. (1970) with some modifications; 4 mL of a sodium methoxide (2 %) solution were added to the fraction, vortexed every 5 min during 20 min at room temperature, then 4 mL of a H₂SO₄ solution (in methanol at 50 %), vortexed a few seconds and vortexed again before adding 2 mL of distilled water. Organic phase (containing fatty acids methyl esters) was extracted two times with 1 mL of hexane and the solvent was evaporated until dryness under N₂. The residue was resuspended in 0.5 mL of hexane and transferred

to a vial. The FAMES were stored at −80 °C until chromatographic analysis.

Separation and quantification of FAMES was carried out using a gas chromatograph, GC-Agilent 6890 N (Agilent Technologies Spain, S.L., Madrid, Spain) equipped with a flame ionization detector and an automatic sample injector HP 7683, using a Supelco SP-2560 fused silica capillary column (100 m, 0.25 mm i.d., 0.2 µm film thickness, Supelco Inc., Bellefonte, PA, USA). Chromatographic conditions were as follows: initial oven temperature of 120 °C (held for 5 min), first ramp at 5 °C/min to 200 °C (held for 2 min) and a second ramp at 1 °C/min to 230 °C (held for 3 min). The injector and detector were maintained at 260 and 280 °C, respectively. Helium was used as carrier gas at a constant flow-rate of 1.1 mL/min, with the column head pressure set at 37.73 psi. 1 µL of solution was injected in split mode (1:50). The fatty acids were quantified using nonadecanoic acid at 0.3 mg/mL as internal standard, which was added to samples prior to free fatty acid separation. Identification of fatty acids was performed by comparison of the retention times with fatty acid standards supplied by Supelco (Bellefonte, PA, USA) and the results are expressed as mg/100 g of fat.

Volatile compounds

The extraction of the volatile compounds was performed using solid-phase microextraction (SPME). A SPME device (Supelco, Bellefonte, PA, USA) containing a fused-silica fiber (10 mm length) coated with a 50/30 µm thickness of DVB/CAR/PDMS (divinylbenzene/carboxen/polydimethylsiloxane) was used for HS-SPME extraction. The sample was ground with a commercial grinder, a 2.00 g portion was weighed into a 40 mL vial and the vial was screw-capped with a laminated Teflon-rubber disk. The fiber was inserted into the sample vial through the septum and then exposed to headspace. The extractions were carried out in an oven to ensure a homogeneous temperature for sample and headspace. The fiber was conditioned prior to analysis by heating it in a gas chromatograph injection port at 270 °C for 60 min, following the manufacturer specifications. Extraction was performed at 35 °C for 30 min. Before extraction, samples were equilibrated for 15 min at the temperature used for extraction. Once sampling was finished, the fiber was withdrawn into the needle and transferred to the injection port of the gas chromatograph–mass spectrometer (GC–MS) system.

A gas chromatograph 6890 N (Agilent Technologies Spain, S.L., Madrid, Spain) equipped with mass detector 5973 N (Agilent Technologies Spain, S.L., Madrid, Spain) was used with a DB-624 capillary column (J&W scientific: 30 m, 0.25 mm id, 1.4 µm film thickness). The SPME fiber was desorbed and maintained in the injection port at 260 °C during 5 min. The sample was injected in splitless mode. Helium was used as a carrier gas with a linear velocity of 40 cm/s. The

temperature programmed was isothermal for 10 min at 40 °C, raised to 200 °C at a rate of 5 °C/min, and then raised to 250 °C at a rate of 20 °C/min, and held for 5 min: total run time 49.5 min. Injector and detector temperatures were both set at 260 °C. The mass spectra was obtained using a mass selective detector working in electronic impact at 70 eV, with a multiplier voltage of 1953 V and collecting data at a rate of 6.34 scans/s over the range m/z 40–300.

Compounds were identified comparing their mass spectra with those contained in the NIST05 (National Institute of Standards and Technology, Gaithersburg) library, and/or by comparing their mass spectra and retention time with authentic standards (Supelco, Bellefonte, PA, USA), and/or by calculation of retention index relative to a series of standard alkanes (C_5 – C_{14}) (for calculating Kovats indexes, Supelco 44585-U, Bellefonte, PA, USA) and matching them with data reported in literature. The results are expressed as area units (AU) $\times 10^8$ /g of dry matter.

Statistical analysis

For the statistical analysis of the results of physico-chemical properties, lipolysis and volatile compounds an analysis of variance (ANOVA) of one way using IBM SPSS Statistics 19.0 program (IBM Corporation, Somers, NY, USA) was performed for all variables considered in the study. The least squares mean (LSM) were separated using Duncan's *t*-test. All statistical test of LSM were performed for a significance level $P < 0.05$. Correlations between variables were determined by correlation analyses using the Pearson's linear correlation coefficient with above statistical software package mentioned.

Result and discussion

Changes on Physico-chemical Characteristics during the Manufacturing Process of Celta Dry-cured Loin

The changes on the physico-chemical parameters of Celta dry-cured loin during the manufacturing process are shown in Table 2. Statistical analysis showed that pH values were significantly ($P < 0.001$) affected by ripening time ranged between 5.60 and 5.80. The increase on pH values observed in this study could be related with the liberation of peptides, amino acids and ammonia from proteolytic reactions (Virgili et al. 2007).

During the ripening process, water activity gradually declined from an initial value of 0.943 in the seasoning stage to 0.841 at the end of the process, finding significant differences ($P < 0.001$) at different steps of the process. This decrease was more marked at the beginning of dry-ripening stage and it is due to the intense dehydration undergone during the drying-

ripening phase, in fact a_w values displayed a positive correlation with moisture content ($r = 0.900$, $P < 0.01$). The Pearson correlations also indicated that a_w was significantly ($P < 0.01$) related to pH ($r = -0.736$), shear force ($r = -0.927$), hardness ($r = -0.831$) and chewiness ($r = -0.798$).

In line with this, moisture content was also significantly ($P < 0.001$) influenced by the ripening process. The moisture content progressively decreased with processing time because of temperature and relative humidity conditions that occurred during the processing. The values declined from an initial value of 69.24 to 34.04 % at the end of process. This decrease was more pronounced between post-seasoning and the first half of ripening phase, with a mean moisture loss of 27.6 %. The values found at the end of the ripening stage were similar that those reported for dry-cured loins from pure Iberian and from Iberian $\times$ Duroc crossbreeds (mean values of 34.38 vs. 36.26 %, respectively), processed at similar conditions (Muriel et al. 2004a; Ramírez and Cava 2007). It was from Pearson correlation test that moisture contents were also positively ($P < 0.01$) related to instrumental colour parameters of L^* -values ($r = 0.830$), a^* -values ($r = 0.632$) and b^* -values ($r = 0.750$) and negatively correlated to hardness ($r = -0.901$), chewiness ($r = -0.862$) and shear force ($r = -0.884$).

As it was expected, there were no significant differences ($P > 0.05$) in protein and IMF contents, expressed as dry matter, during the manufacturing process of Celta dry-cured loin (Table 2). Regarding protein, the samples showed mean values around 73 % of dry matter. This finding is in agreement with those reported by Ramírez and Cava (2007) who noticed similar mean values of protein in dry-cured loins from Iberian pig crossbreeds (48.28 vs. 47.81 % of wet matter). In relation to IMF content, at the end of the dry-curing process the samples presented mean values of 11.70 % of dry matter. These results were similar to those reported by Muriel et al. (2004a) who observed IMF values of 10.22 % in Iberian dry-cured loin from Lampiño line, whereas this author also showed lower IMF contents in Iberian dry-cured loin from Retinto genotype (6.77 %) and Torbiscal line (7.85 %).

Statistical analysis displayed that instrumental colour parameters (L^* , a^* and b^* -values) were significantly ($P < 0.001$) influenced by processing time, decreasing during whole process (Table 2). The L^* -values ranged from 41.72 to 30.47. The more notable decrease in L^* -values occurred at the end of the process, during the dry-ripening stage, with a mean decrease of 13.07 %. This decrease in L^* -values was related to formation of dark colour in the dry-cured loins due to browning reaction. It was from Pearson correlation test that L^* -values were significantly correlated with a_w ($r = 0.789$, $P < 0.01$) and moisture content ($r = 0.830$, $P < 0.01$). Our mean L^* -values obtained at the end of the dry-curing were lower than those reported by other authors in dry-cured loins matured during 4 months (Campus et al. 2008; Cava et al. 2009; Ramírez and Cava 2007). Regarding a^* and b^* -values, the higher decreases

Table 2 Evolution of physico-chemical parameters during the manufacture of Celta dry-cured loin, results expressed as means $\pm$ standard error ($n=5$)

	Seasoning	Post- seasoning	Dry-ripening (days) 30	SEM 60	P value	
Chemical Composition						
pH	5.62±0.07 ^a	5.60±0.05 ^a	5.79±0.06 ^b	5.80±0.06 ^b	0.024	0.001
Water activity	0.943±0.001 ^c	0.942±0.005 ^c	0.879±0.026 ^b	0.841±0.013 ^a	0.010	0.001
Moisture (%)	69.24±1.03 ^d	57.26±1.99 ^c	41.46±3.00 ^b	34.04±1.79 ^a	3.169	0.001
Intramuscular fat (% of DM)	11.01±1.41	11.02±0.95	10.68±0.58	11.70±0.92	0.225	0.465
Protein (% of DM)	73.16±2.06	72.98±0.71	73.04±0.66	72.49±1.28	0.274	0.859
NaCl (% of DM)	9.03±0.17	8.44±0.19	8.86±0.43	8.69±0.39	0.082	0.064
TBAR’S (mg MDA/kg)	0.07±0.02 ^a	0.13±0.04 ^a	0.23±0.03 ^b	0.34±0.10 ^c	0.026	0.001
Colour Parameters						
Luminosity (L*)	41.72±2.65 ^c	37.71±2.63 ^b	35.05±2.47 ^b	30.47±1.77 ^a	1.060	0.001
Redness (a*)	13.06±1.79 ^b	9.14±0.79 ^a	9.71±1.71 ^a	8.40±1.16 ^a	0.503	0.001
Yellowness (b*)	11.46±2.39 ^b	5.83±0.60 ^a	6.15±0.56 ^a	4.61±1.13 ^a	0.667	0.001
Textural Parameters						
Shear force (kg)	1.04±0.36 ^a	1.33±0.22 ^a	2.34±0.19 ^b	3.21±0.67 ^c	0.214	0.001
Firmness (kg/s)	0.21±0.08 ^a	0.26±0.02 ^a	0.53±0.06 ^b	0.79±0.16 ^c	0.057	0.001
Total work (kg×mm)	8.61±2.51 ^a	12.99±3.84 ^{ab}	16.45±2.48 ^b	22.67±5.89 ^c	1.429	0.001
TPA test						
Hardness (kg)	0.97±0.33 ^a	2.63±0.58 ^b	12.28±1.48 ^c	11.28±2.12 ^c	1.185	0.001
Springiness (mm)	0.59±0.03 ^a	0.60±0.08 ^a	0.69±0.04 ^{ab}	0.62±0.04 ^a	0.013	0.041
Chewiness (kg × mm)	0.28±0.11 ^a	0.86±0.32 ^a	5.17±0.39 ^c	3.98±0.88 ^b	0.483	0.001
Cohesiveness	0.47±0.03 ^a	0.52±0.03 ^b	0.61±0.02 ^d	0.57±0.03 ^c	0.013	0.001

^{a-d} Means in the same row (corresponding to the same parameter) not followed by a common letter differ significantly ($P<0.05$; Duncan test)

SEM is the standard error of the mean

DM Dry matter

occurred at the beginning of the process, with a mean declines of 30.02 and 49.13 %, respectively. The lowest a* and b*-values were found at the end of the dry-ripening process (8.40 and 4.61, respectively), which were much lower than those displayed by the aforementioned authors. On the other hand, the total chlorides content (expressed as g/100 g of dry matter) of the loin pieces was not affected by ripening time and ranged between 9.03 and 8.44 %.

The degree of lipid oxidation in the Celta dry-cured loins was measured by TBARs method which determines the amount of malonaldehyde (MDA) formed in the oxidation process. TBARs values increased significantly ($P<0.001$) during the manufacturing of Celta dry-cured loin from 0.07 to 0.34 mg MDA/kg. The increase in malonaldehyde contents during the post-seasoning stage and during the dry-ripening period could be related to the prooxidant action of metallic ions present as impurities in the salt used in the curing process. Our TBARs values at the end of the dry-ripening process were similar to those obtained in other dry-cured loins from cross-breeds of Iberian pigs (0.29 vs. 0.34 mg MDA/kg) (Ramírez and Cava 2007), but lower than those found in dry-cured loins manufactured from pure Iberian pigs (1.07 vs. 0.34 mg MDA/kg) (Ventanas et al. 2006).

The Warner-Bratzler (WB) test (shear force, firmness and total work) was significantly ($P<0.001$) affected by the ripening period (Table 2). The values of shear force increased with the maturation process from an initial value of 1.04 to 3.21 kg. This behavior could be due to the coagulation of protein at low pH and the decreases of moisture contents that occurred in dry-cured meat products especially during dry-ripening phase (Lorenzo et al. 2012). To this regards, Person correlation test displayed significant ($P<0.01$) correlations between shear force and pH ($r=0.665$), water activity ($r=-0.927$) and moisture content ($r=-0.884$).

Regarding texture profile analysis (TPA) traits, significant differences ($P<0.05$) were also found between these textural parameters (hardness, springiness, chewiness and cohesiveness) and the different maturity levels. The lowest values of the aforementioned parameters were found at the beginning of the ripening (Table 2). As occurred with shear force, hardness increased from 0.97 to 11.28 kg during the process. Chewiness values also increased during ripening period from 0.28 to 3.98 kg $\times$ mm, but was at the beginning of the dry-ripening stage where underwent a more marked increase. These rising values were expected since dry-cured loins become tougher and pasty gummy with the progress of

maturation (Szczesniak 2002). Changes in hardness and chewiness during curing process have been attributed to both water content and state of protein (Lorenzo et al. 2012). At the end of the process, moisture loss from 69.24 to 34.04 % is enough to cause an increase in hardness. In fact, it was found from Pearson correlation test that moisture content was negatively correlated ($P<0.01$) to hardness ($r=-0.901$) and chewiness ($r=-0.862$). Our final values of hardness were slightly lower than those reported by Ramírez and Cava (2007) who found values ranged from 19.28 to 22.34 kg in Iberian dry-cured loin. Finally, springiness and cohesiveness values also increased during ripening process; however, the increases were not so important. The values ranged from 0.59 to 0.62 mm and from 0.47 to 0.57, for springiness and cohesiveness, respectively. It was found from the Pearson test that cohesiveness was significantly ($P<0.01$) correlated to moisture content ($r=-0.768$) and a_w ($r=-0.657$).

Changes on free fatty acid during the manufacturing process of celta dry-cured loin

The evolution of the free fatty acid (FFA) of Celta dry-cured loin during the manufacturing process is summarized in Table 3. Statistical analysis showed that total FFA content were significantly ($P<0.001$) affected by ripening process. Two main stages (seasoning and dry-ripening) could be distinguished in the total FFA content; however a more pronounced increase of the total FFA content occurred during the dry-ripening stage (see Table 3), but mainly along the first half of it [values after

30 and 60 days of dry-ripening were not significantly ($P>0.05$) different]. It was reported that the amount of total FFA increased in other meat products, during the processing, such as dry-cured loins (Ventanas et al. 2006), dry-cured hams (Zhou and Zhao 2007) and dry-cured sausages (Gómez and Lorenzo 2013). The referred increase of total FFA could be the result of muscle lipolytic enzymes (Motilva et al. 1993), with the polyunsaturated fatty acids (PUFA) predominating up to the post-seasoning step and the monounsaturated fatty acids (MUFA) taking that place along the dry-ripening stage. To this regards, Stahnke (1994) observed that during the manufacturing process of fermented sausages, the PUFA are liberated in a higher proportion than the MUFA and SFA, fundamentally because they are originated from the hydrolysis of phospholipids. However, in this study, the MUFA are liberated in greater proportions than the PUFA and SFA, indicating that the liberation also originates from the triglycerides that are richer in monounsaturated fatty acids. The predominant fatty acids were the PUFA in the first phase and the MUFA in the dry-ripening stage (Table 3). In both cases, the values increased with the maturation process from an initial value of 77.82 to 470.20 mg/g of fat and from 54.35 to 478.42 mg/g of fat, for MUFA and PUFA, respectively. These findings are in agreement with those reported by Ramírez and Cava (2007) who observed that MUFA were the predominant fatty acids at the end of the maturation of dry-cured loin.

Regarding PUFA, linoleic acid (C18:2n6c) was the predominant fatty acid. The obtained values were approximately of 89 and 77 % of total FFA from PUFA fraction at the post-

Table 3 Evolution of free fatty (mg/g fat) acids during the manufacture of Celta dry-cured loin, results expressed as means $\pm$ standard error ($n=5$)

Fatty acid	Seasoning	Post-seasoning	Dry-ripening (days)	SEM	P value	
			30	60		
C16:0	12.95 $\pm$ 5.26 ^a	63.19 $\pm$ 14.27 ^b	302.19 $\pm$ 11.99 ^c	319 $\pm$ 34.88 ^c	31.843	0.001
C16:1n9	0.00 $\pm$ 0.00 ^a	0.00 $\pm$ 0.00 ^a	26.44 $\pm$ 6.44 ^b	22.42 $\pm$ 4.33 ^b	2.932	0.001
C18:0	19.30 $\pm$ 5.98 ^a	16.08 $\pm$ 5.87 ^a	135.73 $\pm$ 28.11 ^b	121.77 $\pm$ 17.30 ^b	13.261	0.001
C18:1n9c	54.35 $\pm$ 4.77 ^a	79.11 $\pm$ 12.59 ^b	457.09 $\pm$ 25.07 ^c	456.00 $\pm$ 22.41 ^c	44.913	0.001
C18:2n6c	66.51 $\pm$ 6.72 ^a	103.93 $\pm$ 9.21 ^b	256.42 $\pm$ 14.125 ^c	364.13 $\pm$ 48.44 ^d	27.932	0.001
C18:3n3	0.00 $\pm$ 0.00 ^a	0.00 $\pm$ 0.00 ^a	43.49 $\pm$ 4.80 ^c	21.96 $\pm$ 6.98 ^b	4.231	0.001
C20:4n6	11.31 $\pm$ 3.52 ^a	12.30 $\pm$ 3.25 ^a	36.21 $\pm$ 7.09 ^b	79.53 $\pm$ 12.86 ^c	6.541	0.001
C20:5n3	0.00 $\pm$ 0.00 ^a	0.00 $\pm$ 0.00 ^a	0.79 $\pm$ 0.07 ^b	4.56 $\pm$ 0.83 ^c	0.441	0.001
SFA	32.25 $\pm$ 8.84 ^a	79.28 $\pm$ 19.72 ^b	438.02 $\pm$ 38.88 ^c	441.10 $\pm$ 43.75 ^c	44.650	0.001
MUFA	54.35 $\pm$ 4.77 ^a	79.11 $\pm$ 12.59 ^b	483.53 $\pm$ 28.32 ^c	478.42 $\pm$ 25.09 ^c	47.739	0.001
PUFA	77.82 $\pm$ 7.62	116.24 $\pm$ 8.28	336.92 $\pm$ 18.71	470.20 $\pm$ 67.32	37.737	0.001
Total FFA	164.44 $\pm$ 16.56 ^a	274.64 $\pm$ 27.01 ^b	1258.48 $\pm$ 70.57 ^c	1389.73 $\pm$ 107.06 ^c	128.273	0.001

^{a-d} Means in the same row (corresponding to the same parameter) not followed by a common letter differ significantly ($P<0.05$; Duncan test)

SEM is the standard error of the mean

PUFA= Σ (C18:2n6c+C18:3n3+C20:4n6+C20:5n3)

MUFA= Σ (C16:1n9+ C18:1n9c)

SFA= Σ (C16:0+ C18:0)

seasoning stage and at the end of process, respectively (Table 3). The highest values were found at the end of ripening, with a mean value of 364.13 mg/g of fat. Below in importance was found arachidonic acid (C20:4n6) whose content ranged from 11.31 to 79.53 mg/g of fat during the process, suffering a notable increase from the dry-ripening stage. It was found from Pearson correlation test that PUFA content was correlated to C18:2n6c ($r=0.999$, $P<0.01$) and C20:4n6 ($r=-0.952$, $P<0.01$). Within MUFA, only two fatty acids were detected, namely oleic (C18:1n9c) and palmitoleic (C16:1n9) acids. The predominant was oleic acid, showing levels higher than 95 % of total FFA from MUFA fraction during all the stages of the ripening process. A lower percentage was found in palmitoleic acid, showing values only during dry-ripening stage (around 5 % of total FFA from MUFA fraction) (Table 3). Finally in the SFA, palmitic acid (C16:0) was the most abundant, increasing its content progressively during the maturation process from an initial value of 12.95 to 319.00 mg/g of fat. At the end of the ripening, this fatty acid represented a 72.3 % of total FFA from SFA fraction. The other fatty acid found was stearic acid (C18:0) although in less proportion. Its content was similar during the seasoning and post-seasoning stages and increased suddenly in the dry-ripening phase, from an initial value of 19.30 to 121.77 mg/g of fat.

Changes on Volatile Compounds during the Manufacturing Process of Celta Dry-cured Loin

The average contents of extracted volatile compounds at different processing stages are shown in Table 4. A total of sixty-seven volatile compounds were identified from Celta dry-cured loin samples. The volatile compounds were grouped according to their possible origin as: volatiles derived from spices, microbial activity, lipid oxidation, Maillard reaction and compounds of unknown origin and contaminants. The number of volatile compounds increased during processing, 30 volatile compounds were detected in the seasoning step and 51 in the post-seasoning stage. During the dry-ripening phase, the number of volatile compounds increased, 53 compounds were found after 30 days of dry-ripening and 56 after 60 days of dry-ripening. The obtained results showed that ripening time significantly ($P<0.05$) affected the formation of volatile compounds of Celta dry-cured loin (Fig. 1). Until now there are no studies that evaluate the evolution of volatile compounds during the whole manufacture of dry-cured loin and have not been studied in Celta pig breed. At the end of dry-ripening process, most of the identified volatile compounds derived from microbial activity (66 % of the total area), followed by those originated from spices addition (14.2 % of the total area) and lipid oxidation (11.2 % of the total area), while at the beginning the major volatile

compounds were originated from the addition of spices, with mean values of 57.7 % of the total area (Fig. 1).

Microbial activity could be responsible for the generation of 16 volatile compounds comprising ethyl esters, carbohydrate fermentation and amino acid catabolism (Table 4). At the end of ripening process, ethyl esters compounds were the most abundant reaching around 27 % of the total area of microbial origin. Ethyl esters are formed through esterification of ethanol and organic acids by microbial esterases (Stahnke 1994). Butanoic acid, methyl ester and butanoic acid, 3-methyl, methyl ester were the predominant ethyl esters detected during the manufacturing process of Celta dry-cured loin. Their contents increased during ripening time reaching final values of 11.57 and 21.27 $\times 10^8$ area units, respectively. On the other hand, volatile compounds derived from carbohydrate fermentation represented the second group in importance from microbial activity. Ethanol and 2,3-butanodione were the most abundant volatile compounds originated from carbohydrate fermentation (Sunesen et al. 2001). Finally, 3-methylbutanal was the only volatile compound detected from amino acid catabolism and its content increased with ripening time until 3.97 $\times 10^8$ area units.

In Celta dry-cured loin, volatile compounds from spices were also detected, mainly sulphur compounds and terpenes. The content of these volatile compounds decreased during ripening from 5.7 to 4.8 % of the total area (Fig. 1). These volatile compounds show strong aromatic notes and could play an important role in the overall aroma notes of this meat product (Ramírez and Cava 2007). The contents of sulphur compounds increased during ripening from 5.2 to 15.7 % of the total spices area. Many of them have been previously found in dry-cured sausages in which garlic is an ingredient (Sunesen et al. 2001) and in dry-cured foal loin (Lorenzo 2014a). In the case of terpenes, the contents decreased during manufacture from 24.6 to 9.3 % of the total spices area. Muriel et al. (2004b) suggested that the spices added during the manufacture process are responsible for the origin of these compounds. Compounds derived from added spices lessen the volatiles derived from lipid oxidation, microbial metabolism, and Maillard reactions.

Volatile compounds derived from lipid oxidation were assigned to the following chemical families: alcohols, aldehydes, alicyclic hydrocarbons, aromatic hydrocarbons, ketones and lineal hydrocarbons. Its content increased until 30 days of dry-ripening, from 1.8 to 4.9 % of total area, and then they remained constant till the end of ripening process. These compounds accounted for 11.2 % of the total chromatographic area at the end of the ripening process, which were similar than those found by other authors (Soto et al. 2008). Nevertheless, these outcomes were lower than those reported by Ramírez and Cava (2007) who found that lipid derived compounds accounted for more than 55 % of the total volatiles in Iberian dry-cured loins.

Table 4 Evolution of volatile compounds (chromatographic peak area) during the manufacture of Celta dry-cured loin, results expressed as means $\pm$ standard error ($n=5$)

Compounds (AU x 10 ⁸)	LIR	R	Seasoning	Post-seasoning	Dry-ripening (days) 30	SEM 60	P values	
Spices								
<i>Sulphur compounds</i>								
3-Methylthio-1-propene (allyl methyl sulphide)	731	m	2.49±0.53 ^a	2.52±1.15 ^a	0.00±0.00 ^b	5.80±1.47 ^c	0.574	0.001
3, 3'-thiobis-1-propene (diallyl sulphide)	896	m	0.65±0.14 ^a	2.36±0.48 ^b	3.30±1.21 ^{bc}	3.85±0.32 ^c	0.347	0.001
Dimethyl disulphide	766	m	0.16±0.08 ^{ab}	0.11±0.04 ^a	0.00±0.00 ^a	0.22±0.06 ^b	0.024	0.001
Propylene sulphide (methylthiirane)	611	m	0.00±0.00 ^a	0.14±0.07 ^b	0.00±0.00 ^a	0.16±0.05 ^b	0.022	0.001
<i>Terpenes</i>								
α-Pinene	974	m	0.09±0.03 ^a	0.18±0.02 ^{ab}	0.45±0.14 ^c	0.22±0.03 ^b	0.038	0.001
Camphene	995	m	8.42±2.34 ^a	3.87±2.96 ^b	1.94±0.67 ^b	1.38±0.40 ^b	0.834	0.001
Camphor	1209	m	2.74±0.62 ^a	2.11±0.83 ^a	0.67±0.29 ^b	0.45±0.07 ^b	0.276	0.001
β-Myrcene	1033	m	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.08±0.01 ^b	0.009	0.001
3-Carene	1055	m	0.00±0.00 ^a	0.24±0.06 ^b	0.62±0.08 ^c	0.51±0.19 ^c	0.066	0.001
4-Carene	1120	m	0.07±0.01 ^a	0.08±0.03 ^a	0.13±0.03 ^b	0.08±0.03 ^a	0.009	0.035
Limonene	1072	m	0.27±0.06 ^a	0.61±0.18 ^b	0.76±0.12 ^b	0.57±0.14 ^b	0.054	0.002
Microbial activity								
<i>Ethyl esters</i>								
Acetic acid, methyl ester	582	m, k	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	10.23±2.03 ^b	1.166	0.001
Propanoic acid, 2-methyl-, methyl ester	703	m	0.00±0.00 ^a	0.00±0.00 ^a	7.20±0.45 ^b	3.21±0.16 ^c	0.767	0.001
Butanoic acid, methyl ester	740	m, k	2.61±0.87 ^a	4.91±1.38 ^a	12.87±3.59 ^b	11.57±1.85 ^b	1.22	0.001
Butanoic acid, 3-methyl-, methyl ester	801	m, k	0.06±0.01 ^a	2.44±0.42 ^a	28.64±7.31 ^b	21.27±5.56 ^c	3.305	0.001
Butanoic acid, 3-methyl-, ethyl ester	894	m	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.31±0.05 ^b	0.035	0.001
Pentanoic acid, methyl ester	859	m, k	0.17±0.02 ^a	0.25±0.11 ^a	0.60±0.16 ^b	0.57±0.09 ^b	0.055	0.001
Hexanoic acid, methyl ester	980	m, k	1.08±0.43 ^a	2.09±1.03 ^a	4.46±1.11 ^b	3.62±0.46 ^b	0.385	0.001
Octanoic acid, methyl ester	1161	m, k	0.19±0.07 ^a	0.30±0.12 ^a	0.67±0.31 ^b	0.37±0.04 ^a	0.059	0.011
Benzoic acid, 4-methyl-, 2-trimethyl	1357	m	0.00±0.00 ^a	0.12±0.06 ^b	0.11±0.00 ^b	0.04±0.02 ^a	0.014	0.001
3-hydroximandelic acid, ethyl ester, di-TMS	1155	m	2.64±1.02	1.87±0.41	1.99±0.74	1.97±0.80	0.19	0.503
Propionate methyl	652	m	0.00±0.02 ^a	0.00±0.00 ^a	8.29±1.87 ^b	1.29±0.21 ^a	0.912	0.001
3-Methyl-1-butanol	792	m	0.00±0.00 ^a	0.89±0.09 ^b	7.33±0.53 ^d	1.82±0.64 ^c	0.743	0.001
<i>Carbohydrate fermentation</i>								
Ethanol	608	m	0.00±0.00 ^a	3.61±0.26 ^b	4.72±0.31 ^b	6.81±1.95 ^c	0.676	0.001
Acetic acid	692	m, k	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	2.94±0.55 ^b	0.335	0.001
2,3-butanedione	618	m	0.00±0.00 ^a	0.64±0.12 ^a	23.87±2.74 ^b	4.36±1.34 ^c	2.542	0.001
<i>Aminoacid catabolism</i>								
3-methylbutanal	675	m	0.00±0.00 ^a	3.06±2.29 ^b	4.53±1.37 ^b	3.97±1.54 ^b	0.568	0.006
Lipid oxidation								
<i>Lineal Hydrocarbons</i>								
Hexane	600	m, s, k	2.75±0.46 ^a	3.15±0.47 ^a	0.00±0.00 ^b	3.39±0.43 ^a	0.362	0.001
Nonane	900	m, s, k	0.00±0.00 ^a	0.13±0.06 ^b	0.30±0.05 ^c	0.16±0.03 ^b	0.029	0.001
Decane	1000	m, s, k	0.07±0.01 ^a	1.00±0.29 ^b	2.66±0.77 ^c	0.82±0.19 ^b	0.261	0.001
Undecane	1100	m, s, k	0.09±0.03 ^a	1.04±0.29 ^b	2.47±0.8 ^c	0.54±0.15 ^{ab}	0.253	0.001
Dodecane	1200	m, s, k	0.34±0.14 ^a	0.52±0.13 ^a	1.17±0.43 ^b	0.22±0.07 ^a	0.109	0.001
Tridecane	1300	m, s, k	0.07±0.01 ^a	0.23±0.12 ^b	0.47±0.13 ^c	0.06±0.01 ^a	0.047	0.001
Tetradecane	1400	m, s, k	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^b	0.00±0.00 ^a	0.004	0.001
Heptane, 3-ethyl	886	m	0.00±0.00 ^a	0.12±0.05 ^b	0.31±0.01 ^c	0.09±0.03 ^b	0.03	0.001
Heptane, 3-methyl	910	m	0.00±0.00 ^a	0.00±0.00 ^a	0.44±0.13 ^b	0.00±0.00 ^a	0.051	0.001
Heptane, 2,2-dimethyl	1088	m	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.19±0.03 ^b	0.021	0.001
Heptane, 2,2,4,6,6-pentamethyl	1028	m	0.00±0.00 ^a	0.17±0.06 ^b	0.40±0.16 ^c	0.11±0.03 ^{ab}	0.043	0.001

Table 4 (continued)

Compounds (AU × 10 ⁸)	LIR	R	Seasoning	Post-seasoning	Dry-ripening (days) 30	SEM 60	P values	
Octane, 3-ethyl	999	m	0.00±0.00 ^a	0.05±0.01 ^b	0.13±0.04 ^c	0.00±0.00 ^a	0.015	0.001
Octane, 2,6-dimethyl	1002	m	0.00±0.00 ^a	0.00±0.00 ^a	0.39±0.14 ^b	0.07±0.01 ^a	0.045	0.001
2-nonene	914	m	0.00±0.00 ^a	0.08±0.02 ^b	0.15±0.04 ^c	0.00±0.00 ^a	0.017	0.001
4-nonene, 5-methyl	1008	m	0.00±0.00 ^a	0.12±0.03 ^b	0.19±0.08 ^c	0.08±0.02 ^b	0.02	0.001
3-undecene	1115	m	0.00±0.00 ^a	0.00±0.01 ^b	0.10±0.05 ^c	0.00±0.00 ^a	0.012	0.001
<i>Alicyclic Hydrocarbons</i>								
Propylcyclopentane	843	m	0.00±0.00 ^a	0.00±0.00 ^a	0.10±0.01 ^b	0.00±0.00 ^a	0.011	0.001
<i>Aromatic Hydrocarbons</i>								
1,3-dimethylbenzene	913	m	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.43±0.03 ^b	0.048	0.001
1,2,4-trimethylbenzene	1052	m	0.00±0.00 ^a	0.67±0.32 ^b	0.64±0.13 ^b	0.49±0.17 ^b	0.082	0.001
1-methyl, 4-methylethylbenzene	1077	m	1.90±0.14 ^a	2.95±0.85 ^{ab}	4.32±1.55 ^b	3.23±0.34 ^{ab}	0.301	0.019
1-methyl, 4-(1-methylethenyl)-benzene	1138	m	0.21±0.05 ^a	0.52±0.02 ^b	0.75±0.14 ^c	0.35±0.06 ^d	0.054	0.001
1-ethyl, 3,5-dimethylbenzene	1106	m	0.00±0.00 ^a	0.00±0.00 ^b	0.08±0.01 ^c	0.00±0.00 ^a	0.009	0.001
<i>o</i> -xylene	946	m, k	0.00±0.00 ^a	0.19±0.01 ^b	0.00±0.00 ^a	1.34±0.21 ^c	0.146	0.001
Indane	1096	m	0.00±0.00 ^a	0.00±0.01 ^b	0.09±0.02 ^c	0.00±0.00 ^a	0.01	0.001
<i>Aldehydes</i>								
Hexanal	847	m, s, k	0.00±0.00 ^a	0.29±0.11 ^b	0.00±0.00 ^a	0.00±0.00 ^a	0.034	0.001
3-ciclopentene, 1-acetaldehyde	1188	m	0.33±0.04 ^{ab}	0.45±0.28 ^b	0.17±0.09 ^a	0.10±0.04 ^a	0.049	0.024
<i>Ketones</i>								
2-pentanone	719	m, k	0.20±0.04 ^a	0.56±0.05 ^b	0.69±0.36 ^{bc}	0.93±0.21 ^c	0.083	0.003
2-heptanone	957	m, k	0.00±0.00 ^a	0.00±0.00 ^a	0.26±0.04 ^b	0.00±0.00 ^a	0.029	0.001
2-nonanone	1150	m	0.00±0.00 ^a	0.00±0.00 ^a	0.11±0.01 ^b	0.00±0.00 ^a	0.012	0.001
<i>Alcohols</i>								
3-hexen-1-ol	935	m, k	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.0 ^b	0.07±0.01 ^c	0.008	0.001
Maillard reaction								
2-propanol	597	m	0.70±0.20 ^a	0.87±0.00 ^{ab}	1.27±0.56 ^c	0.79±0.19 ^{ab}	0.09	0.110
Unknown origin and contaminants								
Chloromethane	529	m	0.31±0.22 ^a	0.34±0.11 ^a	0.91±0.43 ^a	5.11±1.28 ^b	0.539	0.001
Ethyl ether	557	m	0.00±0.00 ^a	0.00±0.00 ^a	0.00±0.00 ^a	0.08±0.02 ^b	0.009	0.001
Toluene	785	m, k	0.13±0.03 ^a	0.39±0.01 ^a	0.00±0.00 ^a	2.92±0.77 ^b	0.321	0.001
Bicyclo [3.1.0] hexane, 4-methyl	965	m	0.00±0.00 ^a	0.20±0.08 ^b	0.43±0.12 ^c	0.31±0.07 ^b	0.044	0.001
Bicyclo [3.1.0] hexane, 4-methylene	1024	m	0.00±0.00 ^a	0.12±0.02 ^b	0.18±0.03 ^c	0.14±0.04 ^b	0.019	0.001
Tricyclo [2.2.1.0] heptane	961	m	0.00±0.00 ^a	0.33±0.24 ^b	0.26±0.09 ^b	0.27±0.07 ^b	0.045	0.022
Bicyclo [2.2.1] hept-2-ol	974	m	0.00±0.00 ^a	0.11±0.04 ^b	0.09±0.03 ^b	0.00±0.01 ^c	0.013	0.001

LIR: Linear retention indexes, calculated in relation to the retention time of n-alkane (C₅–C₁₄) series

R: Reliability of identification; k: kovats index in agreement with literature (Lorenzo et al. 2013, 2014b; Purriños et al. 2013); m: mass spectrum agreed with mass database (NIST05); s: mass spectrum and retention time identical with an authentic standard

SEM is the standard error of the mean

^{a-d} Means in the same row (corresponding to the same parameter) not followed by a common letter differ significantly ($P < 0.05$; Duncan test)

Lineal hydrocarbons probably had not important impact on flavor, because they have relatively high odour threshold values (Purriños et al. 2011a, 2011b). These compounds were the most abundant of the volatile compounds derived from lipid oxidation (7.01–19.46 % of the total lipid oxidation area). However, these levels were lower than those obtained by Muriel et al. (2004b) in Iberian dry-cured loins. Within lineal hydrocarbons, the most abundant compounds were hexane,

decane and undecane (Table 4). To this regards, Ruiz et al. (2002) noticed that straight chain hydrocarbons with less than 10 carbon atoms arise mainly from lipid oxidation, while those with longer chains could be accumulated in the fat depots of the animal, probably from feeding (Tejeda et al. 2001).

Aromatic hydrocarbons with origin in lipid oxidation reactions, because of their abundance, could play an important role

Fig. 1 Mean percentage composition of headspace (calculated by the ratio between the sum of peak areas of each group of volatile compounds and the total integrate area) determined by SPME/GC/MS of the different stages of Celta dry-cured loin processing ($n=5$)

in the aroma of dry-cured loin (Ramírez and Cava 2007). They were the second most abundant compounds derived from lipid oxidation, with values that increased with ripening time from 4.45 to 12.32 % of the total lipid oxidation area (Table 4). At the end of manufacturing process, their contents (1.75 vs. 2.15–4.23 % of the total chromatographic area) were lower than those reported by Muriel et al. (2004b). Within aromatic hydrocarbons, 1-methyl, 4-methylethylbenzene was the major volatile compound. Its content increased from 1.90 to 4.32 $\times 10^8$ area units after 30 days of dry-ripening process, and decreased at the end of process till 3.23 $\times 10^8$ area units.

Aldehydes have a great impact on meat product aroma due to their low odour threshold values (Muriel et al. 2004b). Their contents were less than 2 % of the total lipid oxidation area, being 3-ciclopentene, 1-acetaldehyde the most abundant (see Table 4). Within aldehydes, hexanal showed very low levels compared to the results found by Muriel et al. (2004b) and Ramírez and Cava (2007) in Iberian dry-cured loin and by Lorenzo et al. (2014) in Celta dry-cured “lacón”.

Regarding ketones isolated in Celta dry-cured loin, 2-pentanone was the most abundant and its content increased during ripening from 0.20 to 0.93 $\times 10^8$ area units. Other two compounds were also identified, 2-heptanone and 2-nonanone, although in very small amounts and only at 30 days of dry-ripening. 2-ketones may arise from fatty acids by chemical (autooxidation) or enzymatic (β -oxidation) oxidation of free fatty acids by molds (Ramírez and Cava 2007). Furthermore, they are considered to have a great influence on the aroma of meat products and they have been associated with a peculiar aroma, such as ethereal, butter, spicy notes, or molded-surface cheeses (Curioni and Bosset 2002).

Unlike other authors that consider alcohols like the most important chemical group in Iberian dry-cured loin (Muriel et al. 2004b), in the present study, only one alcohol, 3-hexen-1-ol, derived from lipid oxidation was identified and quantified but at trace levels (less than 0.20 % of the total lipid oxidation area), at the end of manufacturing process.

Volatile compounds arising from the Maillard reaction accounted for less than 0.5 % of the total area, so it was the minority group (Fig. 1). To this regards, Mottram (1998) noticed that Maillard compounds which had very low threshold values, can add pleasant aroma notes. In the present study, only 2-propanol was identified in this group and its content increased until 30 days of dry-ripening, from 0.70 to 1.27 $\times 10^8$ area units, and then it decreased in the last step to 0.79 $\times 10^8$ area units.

Finally, the volatiles of unknown origin, significant differences ($P<0.05$) were found among these compounds during ripening time. The values found increased with maturation from 0.1 to 2.7 % of the total area. Seven compounds were assigned to this group, being chloromethane and toluene which presented the highest contents, although their presence could be related to a chromatographic artefact.

Conclusions

The results obtained in this work conducted on dry-cured loin from Celta pig breed indicated that, in general, most of the studied physicochemical, colour and textural parameters were significantly affected by ripening time. As ripening time increased in Celta dry-cured loin, an increasing on TBARs values and hardness was observed. Total FFA increased during the manufacture process, since oleic acid was the most abundant at the end of process followed by palmitic and linoleic. At the end of process, volatile compounds from microbial activity were the most abundant followed by volatile compounds from spices addition and lipid oxidation. The most abundant volatile compound was acetic acid, methyl ester. Flavour formation of dry-cured loin began from post-seasoning stage.

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References

- Bermúdez R, Franco I, Franco D, Carballo J, Lorenzo JM (2012) Influence of inclusion of chestnut in the finishing diet on fatty acid profile of dry-cured ham from Celta pig breed. *Meat Sci* 92:394–399
- Bermúdez R, Franco D, Carballo J, Sentandreu MA, Lorenzo JM (2014a) Influence of muscle type on the evolution of free amino acids and sarcoplasmic and myofibrillar proteins through the manufacturing process of celta dry-cured ham. *Food Res Int* 56:226–235
- Bermúdez R, Franco D, Carballo J, Lorenzo JM (2014b) Physicochemical changes during manufacture and final sensory characteristics of dry-cured celta ham. effect of muscle type. *Food Control* 43:263–269
- Campus M, Flores M, Martínez A, Toldrá F (2008) Effect of high pressure treatment on colour, microbial and chemical characteristics of dry cured loin. *Meat Sci* 80:1174–1181
- Carril JA, Rivero CJ, Fernández M, Lorenzo JM (2013) La raza. In: CETECA (ed) *Manual del Cerdo Celta*. Galicia, Spain, pp 17–41
- Cava R, Ladero L, González S, Carrasco A, Ramírez MR (2009) Effect of pressure and holding time on colour, protein and lipid oxidation of sliced dry-cured Iberian ham and loin during refrigerated storage. *Innov Food Sci Emerg Technol* 10:76–81
- Curioni PMG, Bosset JO (2002) Key odorants in various cheese types as determined by gas chromatography-olfactometry. review. *Int Dairy J* 12:959–984
- Folch J, Lees M, Stanley GHS (1957) A simple method for the insolation and purification of total lipids from animal tissues. *J Biol Chem* 226:497–509
- Franco D, Vázquez JA, Lorenzo JM (2014) Growth performance, carcass and meat quality of the celta pig crossbred with Duroc and Landrace genotypes. *Meat Sci* 96:195–202
- Garrido R, Domínguez R, Lorenzo JM, Franco I, Carballo J (2012) Effect of the length of salting time on the proteolytic changes in dry-cured lacón during ripening and on the sensory characteristics of the final product. *Food Control* 25:789–796
- Gómez M, Lorenzo JM (2013) Effect of fat level on physicochemical, volatile compounds and sensory characteristics of dry-ripened “chorizo” from Celta pig breed. *Meat Sci* 95:658–666
- ISO (1973) Determination of total fat content, ISO 1443:1973 standard. In: *International standards meat and meat products*. Genève, Switzerland
- ISO (1978) Determination of nitrogen content, ISO 937:1978 standard. In: *International standards meat and meat products*. Genève, Switzerland
- ISO (1996) Determination of chloride content-Part 1: Volhard method, ISO 1841-1:1996 standard. In: *International standards meat and meat products*. Genève, Switzerland
- ISO (1997) Determination of moisture content, ISO 1442:1997 standard. In: *International standards meat and meat products*. Genève, Switzerland
- Kaluzny MA, Duncan LA, Merritt MV, Epps DE (1985) Rapid separation of lipids classes in high yield and purity using bonded phase columns. *J Lipids Res* 26:135–140
- Lorenzo JM (2014a) Influence of the type of fiber coating and extraction time on foal dry-cured loin volatile compounds extracted by solid-phase microextraction (SPME). *Meat Sci* 96:179–186
- Lorenzo JM (2014b) Changes on physico-chemical, textural, lipolysis and volatile compounds during the manufacture of dry-cured foal “cecina”. *Meat Sci* 96:256–263
- Lorenzo JM, Temperán S, Bermúdez R, Cobas N, Purriños L (2012) Changes in physico-chemical, microbiological, textural and sensory attributes during ripening of dry-cured foal salchichón. *Meat Sci* 90:194–198
- Lorenzo JM, Bedia M, Bañón S (2013) Relationship between flavour deterioration and the volatile compound profile of semi-ripened sausage. *Meat Sci* 93:614–620
- Lorenzo JM, Franco D, Carballo J (2014) Effect of the inclusion of chestnut in the finishing diet on volatile compounds during the manufacture of dry-cured “Lacón” from Celta pig breed. *Meat Sci* 96:211–223
- Motilva MJ, Toldrá F, Nieto P, Flores J (1993) Muscle lipolysis phenomena in the processing of dry-cured ham. *Food Chem* 48:121–125
- Mottram DS (1998) Flavour formation in meat and meat products: A review. *Food Chem* 62:415–424
- Muriel E, Ruiz J, Martín D, Petron MJ, Antequera T (2004a) Physicochemical and sensory characteristics of dry-cured loin from different Iberian pig lines. *Food Sci Technol Int* 10:117–123
- Muriel E, Antequera T, Petron MJ, Andrés AI, Ruiz J (2004b) Volatile compounds in Iberian-dry cured loin. *Meat Sci* 68:391–400
- Purriños L, Bermúdez R, Franco D, Carballo J, Lorenzo JM (2011a) Development of volatile compounds during the manufacture of dry-cured “lacón” a Spanish traditional meat product. *J Food Sci* 76:C89–C97
- Purriños L, Franco D, Bermúdez R, Temperan S, Carballo J, Lorenzo JM (2011b) Influence of salt content and processing time on sensory characteristics of cooked “lacón”. *Meat Sci* 87:436–442
- Purriños L, Franco D, Carballo J, Lorenzo JM (2012) Influence of the salting time on volatile compounds during the manufacture of dry-cured pork shoulder “lacón”. *Meat Sci* 92:627–634
- Purriños L, Carballo J, Lorenzo JM (2013) The influence of *Debaryomyces hansenii*, *Candida deformans* and *Candida zeylanoides* on the aroma formation of dry-cured “lacón”. *Meat Sci* 93:344–350
- Ramírez MR, Cava R (2007) Effect of Iberian x Duroc genotype on dry-cured loin quality. *Meat Sci* 76:333–341
- Ruiz J, García C, Muriel E, Andrés AI, Ventanas J (2002) Influence on the sensory characteristics on the acceptability of dry-cured ham. *Meat Sci* 61:347–354
- Shehata AJ, de Man JM, Alexander JC (1970) A simple and rapid method for the preparation of methyl esters of fats in milligram amounts for gas chromatography. *Can Inst Food Sci Technol J* 3:85–89
- Soto E, Hoz L, Ordóñez JA, Hierro E, Herranz B, López-Bote C, Cambero MI (2008) Impact to feeding and rearing systems of Iberian pig on volatile profile and sensory characteristics of dry-cured loin. *Meat Sci* 79:666–676
- Spanish Regulation (2008) Real Decreto 2129/2008, de 26 de diciembre, por el que se establece el Programa Nacional de Conservación, Mejora y Fomento de las Razas. In: Ministerio de Medio Ambiente, Medio Rural y Marino (ed) *Boletín Oficial del Estado* n°23, 27 de enero de 2009. Spain, pp 9211–9242
- Stahnke L (1994) Aroma components from dried sausages fermented with *Staphylococcus xylosum*. *Meat Sci* 38:39–53
- Sunesen LO, Dorigoni V, Zanardi E, Stahnke L (2001) Volatile compounds released during ripening in Italian dried sausage. *Meat Sci* 58:93–97
- Szczesniak AS (2002) Texture is a sensory property. *Food Qual Prefer* 13:215–225
- Tejeda JF, García C, Petron MJ, Andrés AI, Antequera T (2001) N-alkane content of intramuscular lipids of Iberian fresh ham from different feeding systems and crossbreeding. *Meat Sci* 57:371–377
- Ventanas S, Estévez M, Tejeda JF, Ruiz J (2006) Protein and lipid oxidation in *Longissimus dorsi* and dry cured loin from Iberian pigs as affected by crossbreeding and diet. *Meat Sci* 72:647–655
- Virgili R, Sacconi G, Gabba L, Tanzi E, Soresi Bordini C (2007) Changes of free amino acids and biogenic amines during extended ageing of Italian dry-cured ham. *LWT Food Sci Technol* 40:871–878
- Vyncke W (1975) Evaluation of the direct thiobarbituric acid extraction method for determining oxidative rancidity in mackerel (*Scomber scombrus* L). *Fette Seifen Anstichm* 77:239–240
- Zhou G, Zhao G (2007) Biochemical changes during processing of traditional Jinhua ham. *Meat Sci* 77:114–120