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THE EFFECT OF CATABOLIC TRANSFORMATIONS OF PROTEINS AND FATS ON THE QUALITY AND NUTRITIONAL VALUE OF RAW RIPENED PRODUCTS FROM ZLOTNICKA SPOTTED AND ZLOTNICKA WHITE MEAT*

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Abstract

The aim of the study was to compare the advancement of the ripening as well as catabolic changes in proteins and fats of Zlotnicka Spotted (ZS) and Zlotnicka White (ZW) meat and their impact on the quality and nutritional value of ready-to-eat products. The meat of the breeds ZS and ZW differed not only in the basic chemical composition but also in the susceptibility to catabolic transformations of proteins and lipids, which translated into a separate technological and nutritional quality as well as the profile of volatile odor compounds. Loins due to their compact histological structure, low pH (5.4) and decreased water activity (0.92–0.93) were characterized by a lower number of coagulase-negative cocci (3.3 log cfu/g) compared to hams. The products of both breeds differed in the content of selected neutral glucogenic amino acids with a pI in the range of 5.6–6.1 mainly. The content of biogenic amines was therefore completely dependent on the metabolic potential of acidifying bacteria. Larger number of lactic acid bacilli (7.5–7.7 log cfu/g) and lactic acid cocci (7.9–8.3 log cfu/g), as well as a higher content of saturated (55.2–53.7%) and polyunsaturated fatty acids (6.4–7.0%) shaped the final pH of hams (5.3). Presence of aldehydes, ketones and alcohols indicated existing fat oxidation despite the small values of the TBA index of hams (1.1 mg/kg) and loins (0.4–0.6 mg/kg). The volatile compounds that differentiated products of ZS and ZW formed by the oxidation and microbial activity, were, primarily: octanal, 1-hydroxypropan-2-one, 3-methylpentan-2-one, propane-1,2-diol, 2,5-dimethylfuran and 3-hydroxybutan-2-one, butane-2,3-dione, butane-1,2-diol, respectively.

Key words: Zlotnicka, meat, ripening, catabolism, chemical composition

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Dry-cured meats are precious for their nutritional value and the flavor profile specific for the region of origin (Flores and Toldra, 2011; Kołożyn-Krajewska and Dolatowski, 2012; Węsierska et al., 2013). Biochemical changes such as the enzymatic lysis of proteins, lipids and saccharides, catabolism of their products and physical processes lead to the development of specific sensory properties, guarantee the quality and safety of ready-to-eat products (Leroy et al., 2010; Flores and Toldra, 2011; Latorre-Moratalla et al., 2011). The raw climate of the Warmian-Masurian region and the multiculturalism of the Suwałki has for centuries shaped the local pork meat tradition on the border of Poland, Belarus, Lithuania and Russia. The production process begins with the salting or curing of high quality raw meat by dry, wet or combined method. The obtained products are safe, smoked or non-smoked, dry, unique in terms of sensory impressions, including colour and structure on the cross-section, hardness, juiciness, saltiness and aroma of pork, enriched with a light aftertaste of lactic acid or marinade. In order to restore the full sensory capabilities of Polish raw meat products, this work was based on the meat of native breeds with features characteristic of primitive breeds: Zlotnicka Spotted (ZS) meat-bacon type and Zlotnicka White (ZW) meat type, included in the program for the protection of livestock genetic resources since 2007 by the Polish Ministry of Agriculture and Rural Development (Regulation of 28 February 2008). ZS differs from the ZW by a slow growth rate, late ripening, poorly muscled body conformation, short and flat ham. The average carcass meatness of ZS is 50%. Pigs do not deposit intramuscular fat but in the form of lard. They are cultivated most often on organic farms with extensive rearing methods. ZW produces meat with marbled muscle tissue, useful for the production of regional meats (Janiszewski et al., 2015). The average meatness is 55.1%. On 12 May 2006, Zlotnicka meat was registered on the Polish list of traditional products. Until now, several products have been registered by the Ministry of Agriculture and Rural Development, including "Wielkopolska Pork Zlotnicka" (2006), "White sausage in a jar" (2007) made from meat of ZS and "Leg roasted from a Zlotnicka White pig" (2007) (Krupiński, 2011). In the European Union, traditional products made from the meat of native pig breeds are highly appreciated: the Spanish "ibérico" ham, Tuscan "cinta senese", Basque ham and the Corsican "prisuttu", produced respectively from Iberian, Cinta Senese, Pie Noir du pays Basque and Corsican Black or Corsican Spotted pig meat (www.slowfood.com). In spite of greater fatness in relation to ZW, the ZS meat can be intended for the production of smoked meats, especially dried, which constitute a range of local products associated with a specific region (Fabri and Bergonzini, 1981; Kapelański et al., 2006; Cebulska, 2018). Debrecéni et al. (2018) claim Polish indigenous pig breeds are more suitable for the production of special meat products due to acceptable fattening and meat quality. The aim of the study was to compare the basic chemical composition, physicochemical properties including WB shear force, TPA parameters, pH and water activity, quantitative and qualitative composition of denitrifying and acidifying microflora as well as free amino acids, biogenic amines, fatty acids and volatile compounds profiles of dry-cured traditional hams and loins, produced from the meat of native Polish Zlotnicka Spotted and Zlotnicka White breeds.

Material and methods

Dry-cured products manufacture

The raw material used comprised hams (H) and loins (L) of native pigs ZS (HZS, LZS) and ZW (HZW, LZW). The topside was taken for hams as well as *m. longissimus thoracis* for loins production. Three times, after reaching the slaughter mass, selected pigs were disconnected from the herd and slaughtered. The meat was collected from each batch, therefore the production was repeated three times. Each time, the meat came from the same litter of pigs (half-siblings, the average weight: 125–130 kg). All activities related to slaughter and post-slaughter processing were carried out in an industrial slaughterhouse in accordance with applicable regulations. The cuts for production were randomly selected from a pool of 30 carcasses. The weight of elements after boning varied between 0.9 and 1.3 kg. After the embrocation with a mixture of 2% of non-iodized salt, 1% of curing salt (min. 98.4% NaCl, 0.6% $NaNO_2$, Anna, Poland), 0.3% of sugar and spices (0.9% of juniper berries, 0.4% of allspice, 0.4% of pepper, 0.4% of garlic) in relation to the meat weight, the elements were placed in containers for curing in dry (2 weeks) and then wet conditions (1 week) at 4–7°C. The wet curing method allowed the penetration of relatively small pieces of meat. The ratio of the amount of the brine to the meat was 2 : 3. The 8° brine contained 87 g of NaCl per 100 mL of water. The cooled cure was slightly boiled before to eliminate any accidental microflora. Meats were smoked cold three times (15–25°C) with alder-beech chips in daily intervals (8 h/day). Ripening at a temperature of 10–12°C and 85–90% relative humidity (first week) and 85% (subsequent time of ripening) was carried out in a climate chamber KK350TOP+ (POL-EKO) for two (loins) and four (hams) weeks. Three batches were produced. Three products, as the replications in each batch, were immediately distributed to the laboratory for analysis for up to 24 h. Three samples from each product were analyzed.

Sampling

Samples of the raw meat were collected after dry salting and the smoking procedures (ripening period: 0) and at different times throughout the ripening process, due to the properties of the raw material – hams after 2nd and 4th week and loins after 1st and 2nd week. The material for analysis was cut into 1.5 cm thick slice. The first one (external) was rejected because of its significant water loss. After separating the material for the chemical composition (the content of water, protein, fat, ash, salt, free amino acids, free amine groups, biogenic amines, the profile of fatty acids and volatile compounds), texture (WB shear force, TPA hardness, TPA chewiness), pH and water activity as well as the population size of acidifying and denitrifying microflora were estimated. The content of free amino acids, free amine groups, biogenic amines as well as the profiles of fatty acids and volatile compounds were determined only in the final product, ready for consumption. The remaining parameters were determined successively as the process of ripening and drying of meats progressed.

Basic chemical composition and physicochemical properties

The basic chemical composition was evaluated according to the Polish and European adequate standards. The moisture was determined by drying samples to

their stable weight (PN ISO 1442:2000). The protein content was determined with the use of the Kjeldahl method with the set-type 322 (Büchi, Switzerland) (PN-75-A-04018:1975/Az3:2002). Fat was evaluated with the use of the Soxhlet method with ethyl ether extraction (PN ISO 1444:2000) and the salt content with the use of Mohr's method (PN ISO 1841-1:2002). The energy value of meats was determined by the Atwater specific factors (FAO, 2003). The WB shear force was determined using seven cylindrical samples of 14 mm diameter and 15 mm length cuts. The measurements were carried out using a texturometer TA-XT2 (Stable Micro Systems) and a WB knife with a triangular cut-out. The TPA analysis was conducted as described by Breene (1975) using a TA-XT2 texture analyzer with a 50-mm diameter cylindrical probe. Muscle samples were compressed twice, parallel to the fiber direction to 70% of their original size. The results were compiled with the use of the Stable Micro Systems Texture Expert software for Windows, version 1.05. The pH was measured with pH-meter type CP-411 and electrode type PP-3 (Elmetron, Poland) in water homogenate (meat : water 1 : 3) and water activity (aw) was determined with the LabMaster-aw (Novasina, Switzerland), following the instructions.

Acidifying and denitrifying microflora composition

Analysis for bacteriological examination were done as follows: microbiological analysis of total plate count in mesophilic conditions (Standard Methods Agar, Biomérieux, 30°C/48–72 h; PN-EN ISO 4833:2004/Ap1:2005); lactic acid bacteria (LAB) (MRS Agar, Biomérieux, acetic acid used for pH reducing to 5.4, 30°C/24–48 h, anaerobic chamber with a 20% CO_2 enriched atmosphere Sheldon Manufacturing Inc.), lactic acid cocci (M17 Agar, Biomaxima, 30°C/48–72 h, aerobic conditions) following PN-EN ISO 15214:2002; *Micrococcus sp.* as well as coagulase-negative (CNS) and positive *Staphylococcus sp.* (CPSA) determination (Baird Parker Agar Base, yolk emulsion and sodium tellurite, Biomérieux; cocci classified on the basis of coagulase activity, 37°C/24 h; PN-EN ISO 6888:2001/A1:2004).

Amino acids and biogenic amines profile

The chromatographic separation of free amino acids (FAAs) was performed using Dionex UltiMate 3000 HPLC apparatus (Thermo Scientific, USA). The separation was carried out in a Nova-Pak reverse phase C18 column, 4 μm particle size, 150x3.9 mm (Waters, USA) thermostated at 30°C. The two solvent reservoirs contained the following eluents: (A) acetonitril, (B) HPLC grade water at a flow rate of 0.8 mL min^{-1}. The elution program was: 65% A and 35% B for 1 min, increasing to 80% A and 20% B for 9 min, increasing to 90% A and 10% for 2 min, increasing to 95% A and 5% B for 4 min, holding for 7 min and back to 65% A and 35% B and holding for 5 min. Fluorimetric detection was carried out using excitation and emission wavelengths of 340 nm and 530 nm, respectively. The biogenic amines (BAs) analysis was performed using HPLC in accordance with the method described by Innocente et al. (2007) with modifications: 10 g sample of meat was mixed with 15 mL of 6% trichloroacettic acid (TCA), homogenized for 2 min (1000 rpm) and centrifuged at 14000xg for 20 min at 4°C (MPW Med. Instruments, Poland). The obtained supernatant was collected, filtered through Whatman No. 1 filter paper and

the residue was reextracted by 15 mL of fresh of 6% TCA. The volume of the combined supernatants was completed to 50 mL by 6% TCA. The derivatization process was performed by mixing 1 mL of extract with 1 mL of dansyl chloride acetone solution (10 mg mL^{-1}) and 0.5 mL of saturated $NaHCO_3$ solution. Incubation was carried out at 40°C for 60 min with occasional shaking. BAs were extracted twice using 1 mL of diethyl ether for 10 min. The extracts were dried in the stream of nitrogen and the residue was dissolved in 1 mL of acetonitryle. The solution of BAs standards was prepared by mixing 1 mL of each free base standard solution, containing 0.1 mg mL^{-1} of each BA with 5 mL of dansyl chloride acetone solution. The derivatization and extraction procedure was performed in the same manner as the samples. Free amino groups were evaluated by Kuchroo et al. (1983) method in water (water soluble nitrogen WSN) and in phosphotungstic acid (PTA). The WSN fraction was used as follows: 5 mL of the water-soluble protein fraction was added to 5 mL of 40% trichloroacetic acid (TCA) and stirred on Vortex RS-va10 (Phoenix Instrument, Germany) for 10 min, centrifuged at 12000xg for 10 min in a pre-cooled centrifuge MPW-352R, REF 11457 (MPW Med. Instruments, Poland) at 4°C. Then 2 mL of solution were removed and dried under nitrogen. The obtained residue was dissolved in 1 mL of 20 mM HCl. The chromatographic separation (HPLC) of free amino acids was performed with Dionex UltiMate 3000 (Thermo Scientific, USA) with the use of analytical kit ACCQ Tag (Waters, USA). Separation was carried out in a Nova-Pak reverse phase C18 column, 4 μm particle size, 150x3.9 mm (Waters, USA) thermostated at 37°C. The two solvent reservoirs contained the following eluents: (A) acetate-phospate buffer pH=5.2 and (B) mixture of acetonitrile and water (60:40, v/v) at a flow rate of 1 mL min^{-1}, according to the Waters procedure. Fluorimetric detection was carried out using excitation and emission wavelengths of 250 nm and 395 nm, respectively.

Fatty acids profile and TBA index

The fatty acids (FAs) profile including saturated (SFAs), mono- (MUFAs) and polyunsaturated (PUFAs) was determined by gas chromatography from the fat extracted from the samples of ready-to-eat products (Folch et al., 1957). Trace GC Ultra (Thermo Electron Corporation, Italy) with a column Supelcowax 10 (Sigma-Aldrich, USA) 30 m × 0.25 mm × 0.25 μm were used for the determination. The analysis was carried out under the following conditions: helium carrier gas 1 mL min^{-1}, split flow 10 mL min^{-1}, injector temperature 220°C, detector temperature 250°C, starting temperature of the column (first 3 min) 160°C, increased by 3°C min^{-1} to 210°C and maintained for 25 min. Individual fatty acid methyl esters were identified by comparison to the standard mixture (Supelco 37 Component FAME Mix, Sigma-Aldrich, USA). Thiobarbituric acid (TBA) index was determined by the spectrophotometric method of Rosmini et al. (1996) in the spectrophotometer Helios γ (Thermo Electron Corporation, USA). Absorbance was read at 530 nm. TBA was a reagent in malondialdehyde (MDA) assay.

Volatile organic compounds profile

Volatile organic compounds (VOC) were extracted and analyzed using gas chromatograph mass spectrometer GCMS-QP 2010 Plus (Shimadzu, Duisburg, Japan),

with a 50/30 μm DVB/CAR/PDMS fiber (Supelco, Poland), Zebron ZB-5MSi and ZB-Wax columns 30 m x 0.25 mm x 0.25 μm (Phenomenex, Poland) (Calik et al., 2017). The identification was done using mass spectra libraries: NIST08, NIST08s, FF NSC1.3 and retention indices RI, based on analyses of n-paraffin (Supelco, Poland), compared with values from National Institute of Standards and Technology. Some of VOC were verified by standards (S), and for quantitation, the methyl caproate (internal standard) was used (Sigma-Aldrich Co., USA).

Statistica

The statistical analysis was performed using the Statistica software for Windows, version 13.3 (USA). The effect of the ripening time on the chemical properties, texture parameters and microbiological quality was tested using a one-factor (the ripening period) and two-factor (ripening period and the type of product) analysis of variance (ANOVA) with fixed and orthogonal factors. The Scheffe and Duncan post-hoc tests were used for the comparison of the means ($P<0.05$).

Results

Basic chemical composition and physicochemical properties

The time of ripening significantly influenced the level of the analyzed variables, with the exception of the content of salt and the WB shear force (Table 1). The interactions between the type of product and the ripening period were significant ($P<0.05$) for the water, protein, fat and ash content as well as TPA hardness, chewiness and pH. HZS were characterized by a higher fat content ($P<0.05$) and values of energy as well as a lower protein content ($P<0.05$) (7.5%, 833 kJ/198 kcal, 27.6%, respectively) in comparison with HZW (4.9%, 760 kJ/180 kcal, 29.5%, respectively). Due to the greater marbling and intramuscular fat content (6.6%) LZW gave a slightly higher value of energy (866 kJ/206 kcal) than LZS (813 kJ/194 kcal) with the 6.5% fat share. The loins of both breeds differed significantly only in protein content ($P<0.05$). The high content of LZW protein (29.6%) increased the values of WB shear force, TPA hardness and TPA chewiness of LZW (1.9 kG/cm^2, 75.7 and 20.8 N, respectively) ($P<0.05$). The analysis of results confirmed a correlation between the water content and the TPA hardness ($r=-0.98$) in all products. The pH values increased ($P<0.05$) from 5.1 (raw material after dry-curing) to 5.3 (ready-to-eat hams) and 5.4 (ready-to-eat loins).

Acidifying and denitrifying microflora composition

The population of LAB was a dominant microflora with the final size estimated at 7.4–7.8 log cfu/g (Figure 1). The count of both acidifying groups as well as the total count of bacteria did not change significantly during ripening. The number of CNS increased to final 4.3 log cfu/g ($P<0.05$). There was no CPSA, which was an evidence of production safety. The values of pH significantly correlated with the count of LAB ($r=0.95$) as well as CNS ($r=0.98$). There were noticed the correlations between salt content and simultaneously total count of bacteria ($r=0.96$), CNS ($r=0.98$) and lactic acid cocci ($r=-0.97$).

Table 1. The basic chemical composition and physicochemical parameters in relation to the type of product and the ripening period

Properties	Product (P)				Ripening period (RP)			Interaction		
	HZS	HZW	LZS	LZW				source of variance		
	M	*M*	*M*	*M*	0	1	2	P	RP	P x RP
Basic chemical composition										
water (%)	62.40 a	62.72 a	62.95 a	61.40 a	67.56 a	62.53 b	57.07 b	ns	*	*
protein (%)	27.60 a	29.48 b	27.64 a	29.56 b	24.27 a	18.17 b	32.39 c	*	*	*
fat (%)	7.55 a	4.94 b	6.50 c	6.57 c	5.54 a	6.36 b	7.18 c	*	*	*
ash (%)	4.91 a	4.49 b	4.85 a	4.71 a	4.53 a	4.76 b	4.97 c	*	*	*
salt (%)	4.04 a	3.56 b	4.18 a	4.08 a	3.85 a	3.95 a	4.10 a	*	ns	ns
Physicochemical parameters										
shear force (kG/cm^2)	1.94 a	2.23 a	1.71 a	1.88 a	1.73 a	1.85 a	2.26 a	ns	ns	ns
TPA hardness (N)	71.54 a	67.21 b	61.60 c	75.68 a	58.45 a	65.94 b	82.67 b	*	*	*
TPA chewiness (N)	13.74 a	19.60 b	15.25 ab	20.82 c	10.24 a	18.83 b	22.75 b	*	*	*
pH	5.22 ab	5.19 a	5.31 b	5.29 ab	5.08 a	5.19 b	5.35 c	*	*	*
a_w	0.94 a	0.94 a	0.94 a	0.93 a	0.94 a	0.94 a	0.93 b	ns	*	ns

HZS – Zlotnicka Spotted Ham; HZW – Zlotnicka White Ham; LZS – Zlotnicka Spotted Loin; LZW – Zlotnicka White Loin; *M* – mean; a, b, c – values in rows with different letters differ significantly at $P<0.05$; *F* values of interaction significant at $P<0.05$; n=3.

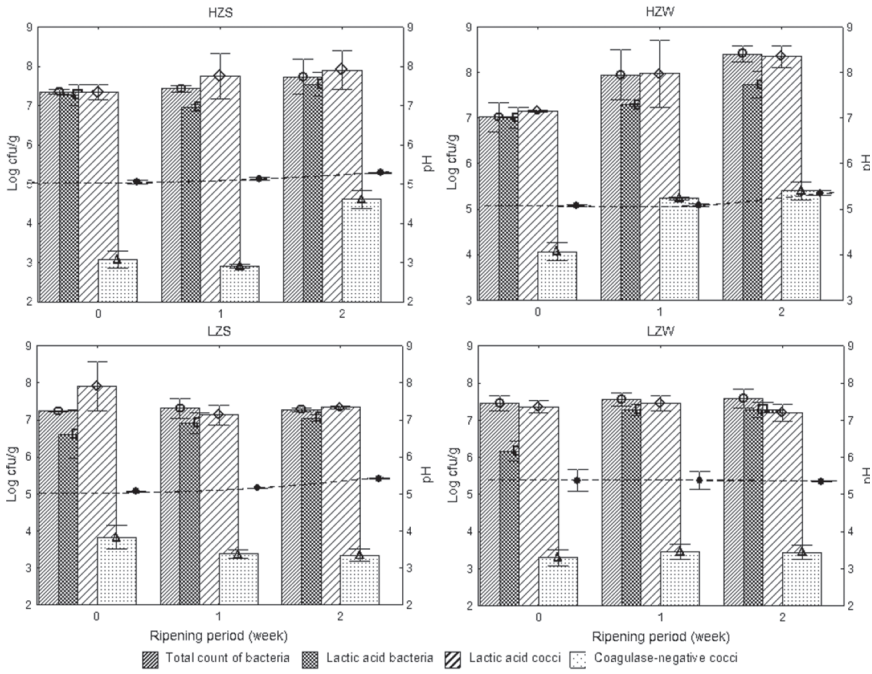

Figure 1. Succession of microflora of ZS and ZW meat products during ripening

Amino acids and biogenic amines profile

The most notable difference in the FAAs composition of ZS and ZW products was noticed in hams ($P<0.05$) (Table 2–3).

They concerned Gln (at about 21.6 mg/kg), Ala (17 mg/kg), Thr (11.9 mg/kg), Pro (9.5 mg/kg), Leu (8 mg/kg) and Asn (7.4 mg/kg). Differences between HZS and HZW at 5 mg/kg were indicated for Gly (at about 5.9 mg/kg), Ile (5.7 mg/kg), Val (5.4 mg/kg), His (5.2 mg/kg) and Met (5.1 mg/kg). Despite smaller values, differences in FAA content in LZS and LZW were significant ($P<0.05$) (Table 3). Differences at the level of 5 mg/kg were indicated for Ala (at about 5.9 mg/kg), Thr (5.5 mg/kg), Glu (5.3 mg/kg) and Leu (5.1 mg/kg). The products of both breeds therefore differed in the FAAs content of selected neutral (except basic His), glucogenic (except ketogenic Leu), polar and non-polar, with a pI in the range of 5.6–6.1 (except His with pI 7.6). The share of neutral glucogenic FAAs could have been an additional factor supporting the development of LAB, not affecting the pH of the environment.

Table 2. The free amino acids and free amine groups profile of dry-cured hams

Product	HZS *M*	*sd*	HZW *M*	*sd*	Product	HZS *M*	*sd*	HZW *M*	*sd*
Free amino acids (mg/kg)					Valine Val	22.69 a	0.89	28.14 b	0.69
Asparagine Asn	4.02 a	0.16	11.47 b	0.95	Methionine Met	18.81 a	0.73	23.91 b	0.59
Serine Ser	32.68 a	1.28	34.70 b	1.13	Lysine Lys	22.92 a	0.90	26.76 b	1.67
Glutamine Gln	23.18 a	0.91	44.82 b	2.82	Isoleucine Ile	19.89 a	0.78	25.63 b	0.75
Glycine Gly	17.14 a	0.67	23.08 b	1.22	Leucine Leu	32.83 a	1.28	40.87 b	1.15
Histidine His	20.65 a	0.81	25.81 b	1.89	Phenylalanine Phe	34.65 a	1.35	31.56 b	1.22
Arginine Arg	84.53 a	1.97	60.04 b	1.84	Total FAA	363.99		472.29	
Threonine Thr	31.78 a	1.24	43.66 b	1.55					
Alanine Ala	30.45 a	1.19	47.45 b	1.17	Free amine groups (g/100 g)				
Proline Pro	21.33 a	0.83	30.87 b	1.08	in H_2O	0.72 a	0.04	0.65 b	0.03
Tyrosine Tyr	30.97 a	1.21	33.56 b	2.57	in PTA	0.08 a	0.01	0.07 a	0.01

HZS – Zlotnicka Spotted Ham; HZW – Zlotnicka White Ham; *M* – mean; *sd* – standard deviation; a, b, c – values in rows with different letters differ significantly at $P<0.05$; n=3.

Table 3. The free amino acids and free amine groups profile of dry-cured loins

Product	LZS *M*	*sd*	LZW *M*	*sd*	Product	LZS *M*	*sd*	LZW *M*	*sd*
Free amino acids (mg/kg)					Valine Val	21.98 a	1,01	25.47 b	0.74
Asparagine Asn	8.30 a	0.38	9.61 b	0.28	Methionine Met	18.64 a	0,86	21.61 b	0.63
Serine Ser	27.58 a	1.27	31.96 b	0.93	Lysine Lys	21.95 a	1,01	25.44 b	0.74
Glutamine Gln	33.09 a	1.53	38.35 b	1.12	Isoleucine Ile	20.27 a	0,94	23.49 b	0.69
Glycine Gly	18.76 a	0.87	21.74 b	0.64	Leucine Leu	32.25 a	1,49	37.38 b	1.09
Histidine His	21.38 a	0.99	24.78 b	0.72	Phenylalanine Phe	25.27 a	1,17	29.29 b	0.86
Arginine Arg	56.39 c	4.27	37.66 d	5.05	Total FAA	373.86		433.28	
Threonine Thr	34.83 a	1.61	40.37 b	1.18					
Alanine Ala	37.05 a	1.71	42.94 b	1.25	Free amine groups (g/100 g)				
Proline Pro	24.62 a	1.14	28.53 b	0.83	in H_2O	0.79 a	0.04	0.73 b	0.03
Tyrosine Tyr	27.89 a	1.29	32.32 b	0.94	in PTA	0.09 a	0.01	0.08 a	0.01

LZS – Zlotnicka Spotted Loin; LZW – Zlotnicka White Loin; *M* – mean; *sd* – standard deviation; a, b, c – values in rows with different letters differ significantly at $P<0.05$; n=3.

The amount of WSN 0.6–0.7 g/100 g ($P<0.05$) determined the majority of typical proteolysis products between products of both breeds. Amino groups dissolved in PTA, 0.06–0.09 g/100 g confirmed the presence of low-molecular fraction of singular FAAs as well as di- and tripeptides. Higher total FAAs content and BAs indicated a greater sensitivity of ZW meat to protein proteolysis and decarboxylation of FAAs. HZS and HZW differed ($P<0.05$) in the share of cadaverine (about 22.5 mg/kg), tyramine (19.0 mg/kg), histamine (12.7 mg/kg) and spermidine (12.0 mg/kg) (Table 4). Despite smaller values, differences in the BAs content in LZS and LZW were significant ($P<0.05$). Histamine, naturally occurring in muscle tissue, reached quite high levels in all products, 150.5–163.2 mg/kg ($P<0.05$) and 101.5–109.0 mg/kg ($P<0.05$), respectively.

Table 4. The biogenic amines profile of dry-cured products

Product	HZS *M*	*sd*	HZW *M*	*sd*	LZS *M*	*sd*	LZW *M*	*sd*
Biogenic amines (mg/kg)								
Tryptamine	6.21 a	0.19	9.08 b	0.56 b	0.11 a	0.01	0.11 a	0.01
Phenylethylamine	1.17 a	0.11	0.25 b	0.01 b	0.03 a	001	0.63 b	0.84
Putrescine	22.98 a	0.69	23.66 a	0.90 a	5.94 a	0.22	6.56 a	0.20
Cadaverine	31.75 a	1.08	54.31 b	3.03 b	22.66 a	2.15	25.88 b	0.60
Histamine	150.52 a	4.27	163.19 b	4.90 b	101.52 a	1.98	109.00 b	0.94
Tyramine	38.18 a	1.31	57.16 b	2.17 b	9.80 a	0.94	11.29 b	0.40
Spermine	2.72 a	0.30	1.94 b	0.07 b	0.78 a	0.03	0.86 a	0.02
Spermidine	22.50 a	1.20	10.47 b	0.43 b	8.09 a	0.29	8.40 a	0.46

HZS – Zlotnicka Spotted Ham; HZW – Zlotnicka White Ham; LZS – Zlotnicka Spotted Loin; LZW – Zlotnicka White Loin; *M* – mean; *sd* – standard deviation; a, b, c – values in rows with different letters differ significantly at $P<0.05$; n=3.

Fatty acids profile and TBA index

The products varied in the participation of selected SFAs (Table 5–6), especially palmitic (C:16) and stearic acids (C:18) ($P<0.05$).

The sum of SFAs in ready-to-eat products was determined at 53.7–55.2% (hams) and 40.1–48.1% (loins). The content of palmitoleic (C16:1 n-7) and vaccenic acid (C18:1n-7) varied hams and loins ($P<0.05$). The mentioned acids influenced the sum of MUFAs, which amounted to 38.4–39.2% (hams) and 48.1–54.5% (loins). Due to different contents of linoleic acid (C18:2n-6) in hams (4.9–5.1%) and in loins (2.6–3.1%), the sum of ω-6 acids was 5.4–5.6% and 2.9–3.4%, respectively. TBA index was determined on the low level of 1.1 mg/kg (hams) and 0.4–0.6 mg/kg (loins). The predominant acid in the ω-3 group was α-linolenic (C18:3n-3), which clearly varied in meat products of ZS (0.6–0.7%) and ZW (1.3–1.7%). The sum of ω-3 acids amounted to 0.8% and 1.5–1.9%, respectively.

Table 5. The fatty acids profile of dry-cured hams

Product	HZS *M*	*sd*	HZW *M*	*sd*	Product	HZS *M*	*sd*	HZW *M*	*sd*
Saturated fatty acids (%)					Polyunsaturated fatty acids (%)				
10;0	0.05 a	0.01	0.06 a	0.02	18;2n-6	5.07 a	0.93	4.89 a	0.67
12;0	0.05 a	0.01	0.05 a	0.01	18;3n-6	0.04 a	0.01	0.04 a	0.01
14;0	0.98 a	0.05	0.95 a	0.00	20;2n-6	0.19 a	0.05	0.18 a	0.04
16;0	33.80 a	4.73	33.11 a	5.71	20;3n-6	0.04 a	0.01	0.04 a	0.01
18;0	19.78 a	3.51	19.13 a	4.43	20;4n-6	0.18 a	0.01	0.21 a	0.04
20;0	0.17 a	0.02	0.18 a	0.01	22;4n-6	0.05 a	0.01	0.06 a	0.00
Σ SFA	55.17		53.74		Σ ω-6	5.57		5.42	
Monounsaturated fatty acids (%)									
14;1	0.02 a	0.01	0.02 a	0.01	18;3n-3	0.67 a	0.36	1.35 a	0.60
16;1n-7	1.62 a	0.09	1.71 a	0.21	20;4n-3	0.03 a	0.01	0.02 a	0.00
16;1n-9	0.68 a	0.06	0.65 a	0.02	20;5n-3	0.02 a	0.01	0.03 a	0.01
17;1	0.13 a	0.03	0.11 a	0.01	22;5n-3	0.03 a	0.01	0.04 a	0.00
18;1n-7	3.23 a	0.65	3.52 a	1.06	22;6n-3	0.01 a	0.01	0.02 a	0.01
18;1n-9	32.19 a	6.56	32.73 a	7.32	CLA	0.08 a	0.01	0.09 a	0.03
20;1	0.52 a	0.17	0.49 a	0.13	Σ ω-3	0.84		1.55	
Σ MUFA	38.39		39.23		Σ PUFA	6.41		6.97	
					TBA (mg/kg)	1.12 a	0.08	1.09 a	0.06

HZS – Zlotnicka Spotted Ham; HZW – Zlotnicka White Ham; *M* – mean; *sd* – standard deviation; a, b, c – values in rows with different letters differ significantly at $P<0.05$; n=3.

Volatile organic compounds profile

VOCs from lipid oxidation, FAAs degradation, smoke treatment and added spices were isolated and identified. Exactly 22 of identified VOCs were chosen as potentially differentiating between the meat products of ZS and ZW (Table 7), among them: octanal, 1-hydroxypropan-2-one, 3-hydroxybutan-2-one (acetoin), butane-2,3-dione (diacetyl), 3-methylpentan-2-one, propane-1,2-diol, butane-1,2-diol and 2,5-dimethylfuran. The PCA-LDA was used to distinguish groups of hams and loins of ZS and ZW breeds, based on the 8 selected volatile compounds, marked in the table. The first two, three, and four principal components accounted for 80.4, 89.8, and 96.9% of the total variance, respectively. These values were very high and allowed to receive also a very good sample distribution with a 100% of classification performance. In the case of properly long ripening, diacetyl would be decomposed by microorganisms into tasteless and odorless compounds. The main source of sulfur compounds and terpenes were garlic and pyrolysis of lignin (Table 8). Furthermore, concentration ranges, odor thresholds, and odor activity values of volatile compounds in dry-cured products were presented in Table 9.

Table 6. The fatty acids profile of dry-cured loins

Product	LZS *M*	*sd*	LZW *M*	*sd*	Product	LZS *M*	*sd*	LZW *M*	*sd*
Saturated fatty acids (%)					Polyunsaturated fatty acids (%)				
10;0	0.06 a	0.01	0.06 a	0.01	18;2n-6	2.64 a	0.11	3.11 a	0.29
12;0	0.05 a	0.01	0.05 a	0.01	18;3n-6	0.02 a	0.01	0.01 a	0.00
14;0	1.03 a	0.05	1.07 a	0.06	20;2n-6	0.08 a	0.02	0.09 a	0.01
16;0	32.19 a	1.00	27.58 b	2.74	20;3n-6	0.02 a	0.01	0.03 a	0.00
18;0	14.53 ab	1.78	11.10 b	2.26	20;4n-6	0.11 a	0.01	0.13 a	0.01
20;0	0.18 a	0.02	0.13 a	0.3	22;4n-6	0.03 ab	0.00	0.02 b	0.01
Σ SFA	48.07		40.12		Σ ω-6	2.90		3.39	
Monounsaturated fatty acids (%)									
14;1	0.03 a	0.01	0.03 a	0.01	18;3n-3	0.63 a	0.41	1.70 a	0.68
16;1n-7	3.01 b	0.27	3.75 b	0.53	20;4n-3	0.02 a	0.00	0.02 a	0.00
16;1n-9	0.59 a	0.01	0.55 a	0.03	20;5n-3	0.02 a	0.01	0.02 a	0.00
17;1	0.09 a	0.01	0.11 a	0.02	22;5n-3	0.02 a	0.01	0.03 a	0.00
18;1n-7	4.42 b	0.16	5.54 b	0.62	22;6n-3	0.02 a	0.01	0.02 a	0.01
18;1n-9	39.43 a	2.20	44.00 a	2.94	CLA	0.11 a	0.02	0.09 a	0.02
20;1	0.49 a	0.00	0.51 a	0.01	Σ ω-3	0.82		1.88	
Σ MUFA	48.06		54.49		Σ PUFA	3.72		5.27	
					TBA (mg/kg)	0.64 b	0.05	0.45 c	0.01

LZS – Zlotnicka Spotted Loin; LZW – Zlotnicka White Loin; *M* – mean; *sd* – standard deviation; a, b, c – values in rows with different letters differ significantly at $P<0.05$; n=3.

Table 7. The profile of potentially differentiating volatile compounds of dry-cured products

Product	HZS *M*	*sd*	HZW *M*	*sd*	LZS *M*	*sd*	LZW *M*	*sd*	Odor impression*	Formation proces	References**
1	2	3	4	5	6	7	8	9	10	11	12
Volatile compounds (ng/g)											
3-Methylbutanal	36.76 a	10.93	12.34 b	1.61	18.86 c	13.84	9.37 d	1.94	Rancid, raw ham, cocoa	Micro. act. (aa cat.)***	Olivares et al., 2009; Corral et al., 2015; Hospital et al., 2015; Degnes et al., 2017
Hexanal	49.73 a	26.51	78.52 b	10.42	1.49 c	1.62	5.51 d	2.58	Aldehydic, fatty, fruity	Lipid oxidation	Corral et al., 2015; Hospital et al., 2015; Gorska et al., 2017
Octanal PC/LD	4.42 a	1.12	2.53 b	0.46	0.60 c	0.41	2.64 b	0.62	Woody, grassy, citrus	Lipid oxidation	Olivares et al., 2009; Corral et al., 2015; Hospital et al., 2015; Gorska et al., 2017
Nonanal	13.12 a	3.79	4.74 b	2.13	3.73 c	1.08	4.48 b	2.38	Polythene, waxy, rose	Lipid oxidation	Corral et al., 2015; Gorska et al., 2017
Heptan-2-one	1.20 a	0.38	1.43 a	0.08	0.55 b	0.09	0.36 b	0.09	Cheesy, banana, leafy	Lipid oxidation	Leroy et al., 2006; Corral et al., 2015; Yalinkiliç et al., 2015; Gorska et al., 2017
1-Hydroxypropan-2-one PC/LD	0.88 a	0.23	2.92 b	0.73	14.44 c	4.98	6.95 d	1.79	Carmellic, burnt	Lipid oxidation	–
3-Hydroxybutan-2-one PC/LD	8.48 a	4.12	154.86 b	24.72	267.12 c	39.45	30.52 d	7.06	Buttery, milky, fatty	Micro. act. (ferm.)	Corral et al., 2015; Hospital et al., 2015; Gorska et al., 2017

Butane-2,3-dione[PC/LD]	0.94 a	0.01	2.02 b	0.68	12.31c	1.55	4.02 d	1.44	Buttery, carmellic	Micro. act. (aa cat., ferm.)	Olivares et al., 2009; Corral et al., 2015; Yim, 2016; Gorska et al., 2017
3-Methylpentan-2-one[PC/LD]	0.03 a	0.06	7.70 b	2.58	0.42 c	0.45	0.00 d	0.00	Peppermint	Lipid oxidation	–
Cyclopentanone	2.10 a	0.80	1.98 b	0.45	4.34 c	1.99	16.18 d	14.28	Minty	Lipid oxidation	Olivares et al., 2009; Narváez-Rivas et al., 2011
2-Methylcyclopentanone	1.61 a	0.66	1.45 b	0.16	3.90 c	2.78	2.65 d	0.77	Roasted beef	Lipid oxidation	Jerkovic et al., 2010; Gorska et al., 2017
2,5-Dimethylcyclopentanone	0.03 a	0.03	0.11 b	0.13	0.24 b	0.23	0.09 b	0.02	Floral, lilac	Micro. act. (keton reduc.)	Jerkovic et al., 2010; Narváez-Rivas et al., 2011
3-Methylbutan-1-ol	55.03 a	15.12	53.32 b	8.14	71.48 c	55.10	34.29 d	7.62	Pungent, fusel, whisky	Micro. act. (aa cat.)	Corral et al., 2015
2-Hexen-1-ol	0.70 a	0.29	0.46 b	0.03	0.35 c	0.45	0.98 d	0.22	Fresh, fatty	–	Narváez-Rivas et al., 2011
Propane-1,2-diol[PC/LD]	8.78 a	2.59	1.41 b	0.17	3.05 c	4.31	1.75 d	1.29	Slightly alcoholic	Reaction of fats with bases	–
Butane-1,2-diol[PC/LD]	218.27 a	47.57	216.63 b	45.63	209.98 c	88.66	37.59 d	19.76	Fruity, creamy, buttery	Micro. act. (aa cat., ferm.)	Corral et al., 2015; Hospital et al., 2015; Ferrocino et al., 2017; Gorska et al., 2017
2,5-Dimethylfuran[PC/LD]	0.30	0.10	0.00	0.00	0.13	0.11	0.26	0.07	Roast beef, bacon	Lipid oxidation	Corral et al., 2015
2(5H)-Furanone	1.23	1.18	0.11	0.06	0.16	0.11	0.36	0.28	Buttery	–	Gorska et al., 2017
Ethyl acetate	15.34	11.04	3.11	0.85	4.41	2.41	5.00	1.33	Rum, cherry	Micro. act. (esterase act.)	Olivares et al., 2009; Corral et al., 2015; Ferrocino et al., 2017

Table 7 – contd.

1	2	3	4	5	6	7	8	9	10	11	12
Ethyl isobutyrate	1.17	0.50	6.02	1.43	6.40	1.22	2.50	0.39	Fruity, alcoholic, fusel	Micro. act. (esterase act.)	Corral et al., 2015
Ethyl 2-methylbutyrate	2.03	0.43	6.50	0.55	5.41	0.85	1.73	0.25	Berry-like, tropical	Micro. act. (esterase act.)	Leroy et al., 2006; Jerkovic et al., 2010; Corral et al., 2015
Ethyl isovalerate	57.43	49.81	61.68	58.89	9.44	1.69	2.34	2.17	Pungent, pineapple	–	Ferrocino et al., 2017

HZS – Zlotnicka Spotted Ham; HZW – Zlotnicka White Ham; LZS – Zlotnicka Spotted Loin; LZW – Zlotnicka White Loin; PC/LD – Principal Component/Linear Discriminant analysis; *M* – mean; *sd* – standard deviation; a, b, c – values in rows with different letters differ significantly at $P<0.05$; n=3.

* Odor impression according to Flavornet (2020); The Good Scents Company; Resconi et al. (2010).

** Confirmation of presence in literature.

*** Microbiological activity (amino acid catabolism, fermentation, ketone reduction, esterase activity).

Table 8. The profile of spices origin volatile compounds of dry-cured products

Product	HZS *M*	*sd*	HZW *M*	*sd*	LZS *M*	*sd*	LZW *M*	*sd*	Odor impression*	Source	References**
1	2	3	4	5	6	7	8	9	10	11	12
Volatile compounds (ng/g)											
α-Thujene	7.06 a	0.75	2.07 b	0.43	125.63 c	33.64	163.10 d	39.19	Woody, herbaceous	Pepper	Fadda et al., 2010; Latorre-Moratalla et al., 2011; Corral et al., 2015
α-Pinene	91.34 a	30.82	27.89 b	2.58	298.67 c	38.00	351.62 d	72.38	Camphoraceous, pine	Pepper	Fadda et al., 2010; Latorre-Moratalla et al., 2011; Corral et al., 2015
Sabinene	76.36 a	27.23	11.81 b	18.31	126.80 c	33.34	134.31 d	48.36	Citrus, camphoraceous	Pepper	–
β-Myrcene	58.55 a	7.11	18.29 b	0.44	203.56 c	50.04	273.90 d	91.87	Woody, rosy, celery	Spices	Latorre-Moratalla et al., 2011; Corral et al., 2015
α-Phellandrene	35.91 a	3.73	12.44 b	1.32	24.53 c	4.04	29.20 d	12.03	Citrus, terpenic,	Pepper	Fadda et al., 2010; Latorre-Moratalla et al., 2011
α-Terpinene	3.87 a	0.25	1.23 b	0.14	37.82 c	12.45	62.08 d	10.66	Thymol, camphoraceous	Spices	Fadda et al., 2010; Corral et al., 2015
Limonene	257.12 a	14.10	100.19 b	3.08	190.84 c	16.61	229.62 d	77.18	Menthol, orange	Pepper	Fadda et al., 2010; Jerkovic et al., 2010; Corral et al., 2015; Bartkiene et al., 2017
γ-Terpinene	36.92 a	5.14	11.76 b	0.59	73.72 c	23.33	114.20 d	31.83	Woody, terpenic, lime	Pepper	Fadda et al., 2010; Corral et al., 2015
Caryophyllene	92.22 a	18.18	18.47 b	1.73	19.56 c	1.96	27.86 d	11.08	Pepper, camphoraceous	Spices	Corral et al., 2015
Camphor	31.20 a	7.25	17.10 b	1.19	1.29 c	0.17	1.31 c	0.53	Camphoraceous	Spices	Corral et al., 2015

Table 8 – contd.

1	2	3	4	5	6	7	8	9	10	11	12
Linalool	382.90 a	36.53	211.08 b	37.54	23.66 c	3.52	21.38 d	9.58	Orange, rose, waxy	Spices	Fadda et al., 2010; Corral et al., 2015
Geraniol	1.83 a	0.87	0.07 b	0.13	0.02 b	0.02	–	–	Rosy, citrus nuances	Spices	–
cis-Myrtenol	–	–	0.43 a	0.38	0.08 b	0.01	0.11 b	0.05	Pine, mint, medical	Spices	–
Eugenol	40.32 a	8.29	30.58 b	4.39	2.75 c	0.63	3.04 d	1.82	Clove, ham, bacon	Spices	Latorre-Moratalla et al., 2011; Corral et al., 2015
Methylthiirane	69.23 a	3.02	75.16 b	8.67	0.73 c	0.16	0.17 d	0.12	–	–	Fadda et al., 2010; Latorre-Moratalla et al., 2011
Allyl methyl sulfide	50.51 a	3.42	40.74 b	11.25	0.57 c	0.30	0.39 d	0.12	Sulfuric, alliaceous	Garlic	Fadda et al., 2010; Latorre-Moratalla et al., 2011
Diallyl sulfide	180.67 a	87.54	72.14 b	47.94	–	–	1.47 c	2.27	Alliaceous, metallic	Garlic	Fadda et al., 2010
Allyl methyl disulfide	20.63 a	16.86	30.77 b	4.91	0.08 c	0.01	0.07 c	0.06	Alliaceous	Garlic	Fadda et al., 2010; Latorre-Moratalla et al., 2011
Diallyl disulfide	349.64 a	41.70	213.31 b	54.17	–	–	–	–	Green onion meaty	Garlic	Fadda et al., 2010; Ferrocino et al., 2017
Allyl propyl disulfide	7.48 a	1.46	4.39 b	1.24	–	–	0.01 c	0.02	Strong onion	Garlic	Latorre-Moratalla et al., 2011
Diallyl trisulfide	2.80 a	1.28	1.30 b	0.51	0.01 c	0.01	0.01 c	0.01	Onion, metallic	Garlic	Fadda et al., 2010; Kaban and Bayrak, 2015
3-Vinyl-1,2-dithiacyclohex-4-ene	1.36 a	0.08	4.14 b	0.54	0.30 c	0.06	0.20 d	0.09	–	Garlic	–
2-Methylfuran	2.57 a	2.88	4.43 b	0.65	1.37 c	0.23	0.86 d	0.27	Acetonic, leafy, cocoa	Spices	Bartkiene et al., 2017

HZS – Zlotnicka Spotted Ham; HZW – Zlotnicka White Ham; LZS – Zlotnicka Spotted Loin; LZW – Zlotnicka White Loin; *M* – mean; *sd* – standard deviation; a, b, c – values in rows with different letters differ significantly at $P<0.05$; n=3.

*Odor impression according to Flavornet (2020); The Good Scents Company; Resconi et al. (2010).

**Confirmation of presence in literature.

Table 9. Concentration, odor thresholds, and odor activity values of potentially aroma-active compounds of dry-cured products

Compound	Concentration (μg/g)		OT** (μg/kg)	OAV***		Compound	Concentration (μg/g)		OT** (μg/kg)	OAV***	
	min*	max*		min	max		min*	max*		min	max
1	2	3	4	5	6	7	8	9	10	11	12
3-Methylbutanal	9.37	36.76	0.15	62.5	245.1	α-Thujene	2.07	163.1	no data	–	–
Hexanal	5.51	78.52	4.5	1.2	17.4	α-Pinene	27.89	351.62	6	4.6	58.6
Octanal	0.6	4.42	0.587	1.0	7.5	Sabinene	11.81	134.31	37	0.3	3.6
Nonanal	3.73	13.12	1	3.7	13.1	β-Myrcene	18.29	273.9	1.2	15.2	228.3
Heptan-2-one	0.36	1.43	24	0.0	0.1	α-Phellandrene	12.44	35.91	4	3.1	9.0
1-Hydroxypropan-2-one	0.88	14.44	10000	0.0	0.0	α-Terpinene	1.23	62.08	80	0.0	0.8
3-Hydroxybutan-2-one	8.48	267.12	800	0.0	0.3	Limonene	100.19	257.12	10	10.0	25.7
Butane-2,3-dione	0.94	12.31	0.059	15.9	208.6	γ-Terpinene	11.76	114.2	260	0.0	0.4
3-Methylpentan-2-one	0	7.7	41	0.0	0.2	Caryophyllene	18.47	92.22	150	0.1	0.6
Cyclopentanone	1.98	16.18	9300	0.0	0.0	Camphor	1.29	31.2	250	0.0	0.1
2-Methylcyclopentanone	1.45	3.9	no data	–	–	Linalool	21.38	382.9	6	3.6	63.8
2,5-Dimethylcyclopentanone	0.03	0.24	no data	–	–	Geraniol	–	1.83	3.2	–	0.6
3-Methylbutan-1-ol	34.29	71.48	220	0.2	0.3	cis-Myrtenol	–	0.43	7	–	0.1
2-Hexen-1-ol	0.35	0.98	100	0.0	0.0	Eugenol	2.75	40.32	0.7	3.9	57.6
Propane-1,2-diol	1.41	8.78	340000	0.0	0.0	Methylthiirane	0.17	75.16	no data	–	-
Butane-1,2-diol	37.59	218.27	70000	0.0	0.0	Allyl methyl sulfide	0.39	50.51	22	0.0	2.3
2,5-Dimethylfuran	0	0.3	no data	–	–	Diallyl sulfide	–	180.67	32.5	–	5.6
2(5H)-Furanone	0.11	1.23	no data	–	–	Allyl methyl disulfide	0.07	30.77	no data	–	–

Table 9 – contd.

1	2	3	4	5	6	7	8	9	10	11	12
Ethyl acetate	3.11	15.34	5	0.6	3.1	Diallyl disulfide	–	349.64	30	–	11.7
Ethyl isobutyrate	1.17	6.4	0.02	58.5	320.0	Allyl propyl disulfide	–	7.48	no data	–	–
Ethyl 2-methylbutyrate	1.73	6.5	0.063	27.5	103.2	Diallyl trisulfide	0.01	2.8	no data	–	–
Ethyl isovalerate	2.34	61.68	0.02	117.0	3084.0	3-Vinyl-1,2-dithiacyclohex-4-ene	0.2	4.14	no data	–	–
						2-Methylfuran	0.86	4.43	200	0.0	0.0

* Minimum and maximum of mean values from product groups.
** Odor thresholds in water (van Gemert et al., 2011).
*** Odor activity value – quotient of the concentration to the odor threshold value.

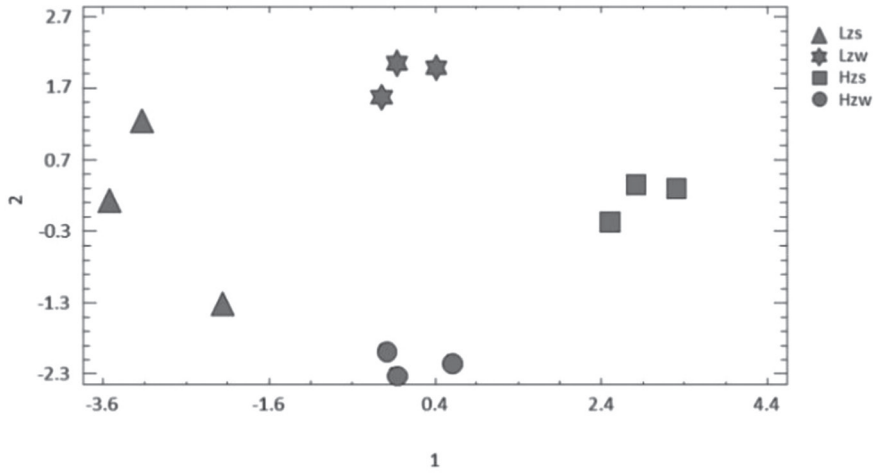

Figure 2. PCA-LDA scatter plot based on semi-quantitative analysis of selected 8 volatile compounds (ng/g) in ready-to-eat raw loins (group 1) and hams (group 2). Each point represents the sample analyzed in duplicate as average

Discussion

The pH<5.8 is the cause of the water loss (reduction of water absorption, drying) and the increase of the content of other chemical meat components (Leroy et al., 2006, 2010; Ordóñez et al., 2010; Olivares et al., 2010). According to Szyndler-Nędza et al. (2017) and Cebulska (2018), ZW and ZS pigs provide the meat with a protein content at a level of 21.7–24.5% and 22.1–25.2%, respectively. The carcasses of ZS, despite the increased fatness, have fat with a thickness similar to commercial crossbreds (Tyra et al., 2015; Szyndler-Nędza et al., 2017; Cebulska, 2018). Maintaining proper proportions between protein and fat is substantial in meat processing. Reports of Kemp et al. (2010), Olivares et al. (2010) and Węsierska et al. (2014) show that the increase in protein and salt content during ripening results in an increase of the texture and nutritional values. The share of IMF gives the impression of juiciness and reduces the hardness of the meat. The results of microbiological analysis of ZS and ZW dry-cured products confirm the literature reports (Spaziani et al., 2009; Latorre-Moratalla et al., 2011; Ravyts et al., 2012; Martínez-Onandi et al., 2016; Bartkiene et al., 2017; Berardo et al., 2017) that difficult conditions (increased salinity and acidity, reduced water activity) allow the growth of the desired microflora, including acidifying (*Aerococcaceae, Enterococcaceae, Lactobacillaceae, Leukonostocaceae, Streptococcaceae*) and halophilic denitrifying cocci (*Staphylococcaceae*, *Micrococcaceae*), supporting the formation of colour (reduction of nitrates (V) to (III), production of catalase and production of lactic acid), sensory profile (proteolysis, lipolysis, catabolism of free amino acids and fatty acids, production

of lactic acid), texture profile (proteolysis, lipolysis, catabolism of free amino and fatty acids, production of lactic acid) and safety (production of lactic acid, bacteriocins and hydrogen peroxide). The increase in the size of the cocci population in the second half of hams ripening complies with the scenario of ripening, which assumes that fermentation of saccharides (development of acidifying bacteria) proceeds most intensively in the first 3–5 days and the proper ripening (development of denitrifying microflora) for a further several weeks (Ravyts et al., 2012; Węsierska et al., 2013; Kaban and Bayrak, 2015). Smoke activity cannot be excluded with reference to the more sensitive microflora (Martínez-Onandi et al., 2016; Marušić Radovčić et al., 2016; Bartkiene et al., 2017). Abellán et al. (2018), Bermúdez et al. (2014) and Chang-Yu et al. (2017) noted similar results analyzing traditional hams and loins, although in the case of loins the results obtained in this study are almost twice lower. The total FAAs content of LZS and LZW reached the values of 373.86 and 433.28 mg/kg, respectively compared with the literature (1096.54 mg/kg). Flores et al. (1997) as well as Toldrá et al. (2000) proved that salt affects exopeptidase activity, including arginine aminopeptidase, hence probably high Arg results (60–84.5 mg/kg) at salt content of 3.6–4.2% in ZS and ZW ripened products. Relatively high levels of certain BAs were reported to indicate the deterioration of food products and/or their defective manufacture. The most important – both qualitatively and quantitatively are histamine, tyramine, putrescine, cadaverine and β-phenylethylamine, products of the decarboxylation of histidine, tyrosine, ornithine, lysine and β-phenylalanine, respectively. The production of BAs in raw meat products is associated mainly with the activity of LAB (Spano et al., 2010). The pathway seems to be strain dependent rather than species specific, suggesting that horizontal gene transfer allows them to spread in the population of LAB (Coton and Coton, 2005; Spano et al., 2010). In addition, the enzymes of pathways involved in BAs production can be encoded by unstable plasmids (Lucas et al., 2005; Satomi et al., 2008) and only strains with amines-related plasmids are able to produce them. The content of BAs in the studied products was therefore completely dependent on the metabolic potential of acidifying bacteria with a count >7 cfu/g. Research confirms that the content of SFAs, MUFAs and PUFAs in pork of both Zlotnicka breeds depends on the composition of the genotype, feed mix and breeding method (Debrecéni et al., 2018; Migdał et al., 2017; Cebulska, 2018). Migdał et al. (2017) and Cebulska (2018) indicated significant differences in the content of palmitic, oleic acids as well as LA, ALA, GLA, AA and DHA. Cebulska (2018) additionally detailed the ZS meat with the content of oleopalmitic, vaccenic and adrenic acids. Probably because of this reason as well as due to the antioxidative activity of wood pyrolysis and spices, the value of the TBA index was determined on the low level of 1.1 mg/kg (hams) and 0.4–0.6 mg/kg (loins). Based on the comprehensive observations of Olivares et al. (2010), Wójciak and Dolatowski (2012) as well as Martínez-Arellano et al. (2016) the salt concentration of 3–4%, pH>4.5<6.0 as well as the concentration of hydrogen peroxide rising as a result of LAB activity are able to increase the enzymatic oxidation and to impart the flavour in this way. On the other hand, the catalase and peroxidase produced by cocci as well as antioxidant components of wood pyrolysis could sufficiently stabilize the meat and fat components during ripening (Kołożyn-

Krajewska and Dolatowski, 2012). It is important to bear that MDA is ready to further transformations such as condensation, reactions with released amino acids, and decomposition by the following catalysts: *Pediococcus acidilactici, Lactobacillus plantarum, Staphylococcus carnosus* (Olivares et al., 2009). Spaziani et al. (2009), Fadda et al. (2010), Ravyts et al. (2012) and Berardo et al. (2017) indicated aldehydes, ketones and alcohols described as secondary products of hydrolytic rancidity and autooxidation of UFAs. Some of them could be the products of microbial metabolism, including carbohydrate fermentation as well as FAAs catabolism or esterification (Martínez-Arellano et al., 2016). Longer chains of fatty acids (C14–C18) could become with products of proteolysis the precursors of selected VOC. According to Leroy et al. (2010), Olivares et al. (2010), Węsierska et al. (2013) and Majcher et al. (2015) the substances obtained in the enzymatic (20%) and non-enzymatic oxidation of UFAs (80%) became the basis for aroma precursors. As it is known, volatile compounds developed from autooxidation of lipids give food rancid or oxidised descriptors, depending on the reached level of oxidation. However, there was no high content of compounds that would adversely change the sensory profile of the tested products. The cause could have been the antioxidative activity of phenols supplied during smoking and absorbed by the surface. Nineteen of 45 volatile compounds (Table 9) were present at the concentrations greater than the suitable odor threshold values (odor activity values, OAV >1). Therefore, the most aroma-active compounds in the products (OAV>100) seemed to be: ethyl isovalerate, ethyl isobutyrate, and 3-methylbutanal, followed by β-myrcene, butane-2,3-dione, and ethyl 2-methylbutyrate. Less odor impacted compounds (OAV between 10 and 100) were: linalool, α-pinene, eugenol, limonene, hexanal, nonanal, and diallyl disulfide. Other potentially odor-active compounds had lower odor activity values (OAV between 1 and 10). These were: α-phellandrene, octanal, diallyl sulfide, sabinene, ethyl acetate, and allyl methyl sulfide. All of above mentioned volatile compounds were food key odorants, found in 227 food samples by Dunkel et al. (2014). The research of strong aroma-active substances, called key odorants, should be very interesting. It can be assumed that the methods will allow reliably characterizing products of animal origin, contribute to the improvement of culinary quality and contribute to the promotion of regional products with specific taste and aroma properties. Despite the many works released so far (Gąsior and Wojtycza, 2016; Karpiński et al., 2015; Majcher et al., 2015; Lv et al., 2015; Marney et al., 2013; Nicolotti et al., 2013) this kind of research still has a great development potential.

Conclusions

The chemical composition of meat (except the salt, selected biogenic amines as well as selected fatty acids content), the quantitative and qualitative composition of the microflora change significantly during ripening, which translates into significant changes in pH, texture parameters (except the shear force) and the profile of volatile compounds of ready products. The meat of the breeds ZS and ZW differs not only in the basic chemical composition but also in the susceptibility to catabolic transformations of proteins and lipids. The salt concentration of dry-cured hams (3.7–4.1%), despite low pH (5.3), creates better conditions for cocci development (4.6–5.4 log

cfu/g) and acidifying bacteria (7.5–8.3 log cfu/g) than slightly higher concentration of salt in loins (4.2–4.3%), with more acceptable pH (5.4). Loins, due to their compact histological structure and low water activity (0.92–0.93) are characterized by lower total microbial contamination (7.3 log cfu/g) and number of CNS (3.3 log cfu/g). The products of both breeds therefore differ in the content of selected neutral polar and non-polar amino acids with a pI in the range of 5.6–6.1 in majority. The share of neutral glucogenic amino acids can be an additional factor supporting the development of LAB without affecting the pH of the meat. The content of biogenic amines in the studied products are therefore completely dependent on the metabolic potential of acidifying bacteria. A larger count of LAB (>7.0 log cfu/g) as well as a higher SFAs (55.2–53.7%) and PUFAs content (6.4–7.0%) and only lower MUFAs (38.4–39.2%) shape final pH values of hams at 5.2. The presence of hexanal, octanal, nonanal, heptan-2-one, 1-hydroxypropan-2-one, 3-methylpentan-2-one, cyclopentanone, 2-methylcyclopentanone and propane-1,2-diol indicates an increased activity of secondary fat oxidation products despite the small values of the TBA index. The amount of products of saccharides fermentation as 3-hydroxybutan-2-one, butane-2,3-dione, butane-1,2-diol and the presence of esters confirm a high enzymatic activity of microorganisms. An undoubted obstacle in the broader description of the quality of raw ripening meats of Zlotnicka Spotted and Zlotnicka White is the limited availability of the raw material. We hope that increasing the interest/attractiveness of the meat of these pigs will popularize pig breeding and increase the availability of raw material for further research. The share of meat products from primitive breeds on the Polish market with a history related to Polish agriculture and breeding should be certain – they are an excellent base for storytelling of the marketing departments of interested plants. On the other hand the new advanced analytical techniques allow evaluating the influence of volatile compounds on the sensory properties. Analysis of the aroma-active substances can be applied to regional and local products, obtained from the native breeds of Poland.

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