Key aroma components of a dry cured sausage with high fat content (sobrassada)

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The key aroma components and the lipolysis in a dry cured sausage "Sobrassada of Mallorca from black pig" were studied. Sobrassada was characterized by a fatty acid profile with a high content of monounsaturated fatty acids and by the generation during the curing process of polyunsaturated free fatty acids that were oxidized to generate flavour compounds. Eighty four different volatile compounds were identified and 3 of them were for the first time detected in dry sausages (methyl nonanoate, 1-methyl-1H-pyrrole and 2-acetyl pyrrole). Thirty five different aroma active zones were found. The aroma of sobrassada was not only due to compounds already detected as essential contributors in dry sausages (3-methyl butanoic acid, ethyl 3-methyl butanoate, 2, 3-butanedione and acetic acid) but also to other compounds such as ethyl octanoate, furfural, benzaldehyde, (Z)-2-nonenal, 4-methyl-phenol, delta-hexalactone, heptanoic acid, 2-pentylfuran and 2-acetyl-pyrrole which gave specific aroma notes.

Keywords: aromas, fermentation, GC-olfactory, fatty acids, sausages

<1>INTRODUCTION

Sobrassada is a dry cured meat product originally made in the island of Mallorca (Spain) consisting of lean pork meat (30-60%), a high percentage of white fat (40-70%) and additives such as curing agents, salt, nitrate and nitrite and spices, such as paprika, pepper, origanum and others (Eim et al., 2008). The development of the typical sensory characteristics is achieved by grinding and kneading the raw materials until a fine paste is obtained and then, the mixture is filled into casing and left to ripen for several weeks under natural or controlled ripening conditions (Rosello et al., 1995). The ripening is performed at temperatures between 14 to 16 ºC and relative humidity between 70-85% while the total ripening time will depend on the product diameter.

Sobrassada was established as a protected geographical indication (PGI) from the island of Mallorca and two different products were defined, Sobrassada of Mallorca and later, Sobrassada of Mallorca from black pig by the Consejo Regulador Sobrassada de Mallorca (http://www.sobrasadademallorca.org). This latest product was defined as a sobrassada exclusively processed using meat from Mallorca black pig and filled into natural casings. It is remarkable the

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aroma of the sobrassada that differs from the aroma detected in other dry cured meat products. The few studies performed in sobrassada have been related with its chemical composition (Rosello et al., 1995), textural properties (Llull et al., 2002a, b) and the addition of fibre (Eim et al., 2008). However, the compounds responsible of its aroma have not been studied.

Research in the aroma of dry cured sausages has identified a high number of volatile compounds (Ansorena et al., 2001; Marco et al., 2006). Several studies determined the contribution of these volatile compounds to the aroma of the sausages using olfactometry techniques that allowed the elucidation of the chemical structures producing the aroma notes (Schmidt and Berger, 1998 a, b; Meynier et al., 1999; Marco et al., 2007). Recently, Söllner and Schieberle (2009) identified 51 key aroma compounds in an Hungarian salami. However, so far there are not studies on sobrassada neither on sobrassada from black pig that can elucidate which are the compounds producing its superior aroma.

Sobrassada is a meat product rich in lipids due to its high content in pork fat. In meat products, the lipids are hydrolysed by lipases generating free fatty acids (Gandemer et al., 2002). During the ripening process, the oxidation of unsaturated free fatty acids generates volatile compounds that affect the flavour of the meat product (Ordoñez et al., 1999). The lipid composition of the meat product as well as the lipolysis process will affect its final flavour that in the case of Sobrassada of Mallorca from black pig could be essential to explain its characteristic aroma.

The production of traditional foods with a protected geographical indication (PGI) not only meets consumer demands for less processed foods, also these products have a high aroma quality. The knowledge of the composition of the key aroma compounds present in sobrassada can help to optimise the manufacture by controlling the generation of the key aroma compounds. Therefore our purpose was to elucidate which are these key aroma compounds in sobrassada of Mallorca from black pig and to study the contribution of the lipolysis to the generation of the key aroma compounds.

<1>MATERIALS AND METHODS

<2>Materials

<3>Sobrassada dry cured sausage samples

Traditional dry cured sausages “sobrassada of Mallorca from black pig”, PGI (El Zagal, Felanitx, Mallorca, Spain) were purchased from a local supermarket. The sausages were manufactured under the traditional specifications. They consisted on pork meat, fat belly, salt, paprika and spices, sugars, sodium nitrite, potassium nitrate and antioxidants; butylhydroxy toluene, butylhydroxy anisole and propyl galate. The sobrassada sausages were dried for approximately 1 month. The weight of each sobrassada sausage was approximately 700 g and the diameter ranged from 50 to 60 mm. Three sausages (S1, S2, S3) from different batches of the same manufacturer were

sliced and directly used for pH, water activity and moisture analyses. Then, the remaining slices were vacuum packed and frozen at -20 ºC for protein, lipid and volatile compound analyses.

<2>Methods

<3>Chemical analyses (pH, water activity, moisture, protein, total lipids)

The pH was measured by introducing a portable pH-meter (HI 99163, Hanna Intruments Inc., Hoonsocket, USA) into a mixture of sobrassada and water (1:1) (ISO 2917, 1974). The water activity (Aw) was analysed using a FAst-lab water activity meter (Gbx, Romans sur Isère Cédex, France), previously calibrated with sodium chloride and potassium sulphate.

Moisture content was determined according to the official method for analysis of meat products BOE (BOE, 1979) by dehydration at 100 ºC until constant weight. Nitrogen content was determined by the Kjeldahl method and protein estimated by multiplying the nitrogen content by 6.25. Total lipids were extracted from 5 g of sobrassada sample according to the method of Folch et al., (1957), using dichloromethane:methanol (2:1) instead of chloroform:methanol (2:1). The extracts were dried in a rotating vacuum evaporator and weighed to determine the total lipid content. The chemical analyses of each sobrassada sample were done in triplicate and results were expressed as the mean in dry matter.

<3>Total fatty acid composition and free fatty acid analysis

Fatty acid methyl esters (FAME) of total lipids were prepared as described by Berry et al. (1965). Free fatty acids were determined in total lipids as described by Gandemer et al. (1991). The free fatty acids (FFA) were separated from the lipid fraction using an ion exchange resin, as described by Needs et al. (1983). Heneicosanoic acid (C21:0) was used as the internal standard. FFAs were converted into FAME using boron fluoride-methanol (Sigma-Aldrich, Chemical Co., Milwaukee, WI) as the methylating reagent. Analysis of the FAME was carried out in a Fisons 816 gas chromatograph (GC) equipped with a flame ionisation detector and a split injector (split ratio used 2:1). The capillary column was a CP-sil 88 (Agilent, Las Rozas, Spain; 100 m, 0.25 mm i.d., 0.2 μm film thickness). The oven temperature program began at 140 ºC for 10 min, ramped to 190 ºC at 4 ºC/min, held at 190 ºC for 10 min, ramped to 220 ºC at 2 ºC/min, held at 220 for 5 min, ramped to 230 at 2 ºC/min and finally, held at 230 ºC for 20 min. Detector and injector temperatures were 240 and 220 ºC respectively. The individual fatty acids were identified by comparing their retention times with those of standard fatty acid methyl esters. For quantification, the response factors of a standard FAME mixture were calculated.

<3>Volatile compounds analysis

Extraction of headspace volatile compounds was done using a solid phase microextraction (SPME) device (Supelco, Bellefonte, PA, USA) with a 85 μm carboxen, polydimethylsiloxane StableFlex fibre (CAR/PDMS SF). For each experiment, 3 g of minced sausage was weighted into a 10 mL headspace vial. The vial was left for 30 min in a thermoblock (J.P., Selecta, Barcelona, Spain) at 37 ºC for equilibration. The CAR/PDMS fibre was then exposed to the headspace for 3 h while maintaining the sample at 37 ºC.

For the identification and quantification of the volatile compounds, a gas chromatograph HP 7890A equipped with an HP 5975C mass selective detector (Hewlett Packard, Palo Alto, CA) was used. The compounds adsorbed by the fibre were desorbed in the injection port of the GC-MS for 15 min at 220 ºC with the purge valve off (splitless mode). The compounds were separated on a DB-624 capillary column J & W Scientific (Agilent Technologies, USA) and analyzed as described Marco et al. (2006). The compounds were identified by comparison with mass spectra from the library database (Nist' 98), kovats retention index (Kovats, 1965) and by comparison with authentic standards. Each volatile compound was quantified using the area of a target ion to avoid coelution. Then, each volatile compound was expressed as the percentage of the total extracted area. The volatile analysis of each sobrassada sample was done in triplicate.

<3>Gas chromatrography-olfactometry

The volatile compounds were adsorbed by the SPME fibre as described above but using 4 g of sobrassada as sample weight. Then, the fibre was desorbed in the gas chromatograph (Agilent 6890, USA) injection port for 6 min at 240 ºC in splitless mode; the split valve was opened after 1 min. The compounds were separated using a DB-624 capillary column (J&W Scientific, 60 m, 0.32 mm i.d., film thickness 1.8 μm). The capillary column was split (2:1) into deactivated and uncoated capillary tubing connected with the sniffing port (ODP3, Gerstel, Mülheim an der Ruhr, Germany) and flame ionization detector (FID), respectively. The sniffing port ODP3 was equipped with a humidified air make up and a computer voice recorder integrated in the Chemstation software (Agilent, USA). Helium was used as the carrier gas with a linear velocity of 35.14 cm/s. Then, the volatile compounds were separated using a temperature programme and after the injection of the fibre the oven was held at 38 ºC for 13 min, ramped at 100 ºC at 3 ºC/min and maintained at 100 ºC during 10 min, then to 150 ºC at 3 ºC/min and to 210 ºC at 5 ºC/min and finally held at 210 ºC for 20 min, the total run time was 82.3 min. Detector temperature was set at 240 ºC.

The detection frequency method was used to estimate the aromatic impact of each volatile compound (Linssen et al., 1993; Pollien et al., 1997). Three trained assessors evaluated the odours from the GC-effluent. A total of 6 assessments were carried out. For each assessment, evaluation of the odour took place over two different time intervals (0-35 and 35-70 min) in order to avoid olfactory fatigue of the assessors. The final detection frequency value (DF) for each compound was obtained by summation of the 6 sniffings. Aroma compounds were identified by three different ways; comparison

with mass spectra and Kovats retention indices (Kovats, 1965); comparison with the retention times of authentic standards injected in the GC-FID; and by coincidence of the assessors descriptors with those in the *Fenaroli's handbook of flavour ingredients* (Burdock, 2002) and in the Flavournet (Acree and Arn, 2004).

<3>Statistical analysis

The differences among the sobrassada sausages were determined by one-factor analysis of variance (ANOVA) using the statistic software Statgraphics plus (v 5.1). Significant effects were compared using Fisher's least significant difference (LSD) test.

<1>RESULTS AND DISCUSSION

<2>Compositional data

The three Sobrassada of Mallorca from black pig batches have similar protein and fat contents which ranged from 12.7 to 15.3% protein and 55.1 to 57.6% fat (Table 1). The batch S1 contained higher significant humidity content than the other batches and also it was observed a higher water activity value in S1 than in the others. There were no differences in pH value among batches. These values are in accordance with the values recommended for the PGI which indicate a pH value lower than 4.5 or water activity lower than 0.91.

<2>Free fatty acids and lipolyisis

Total fatty acid composition in Sobrassada of Mallorca from black pig was not different among batches (Table 2). The three batches were not different in the three main groups of fatty acids (saturated, monounsaturated and polyunsaturated). The main acids were palmitic (23%), stearic (10%), oleic (50%) and linoleic (8%). Total saturated fatty acids were about 34-35%, monounsaturated 54-55% and polyunsaturated 10%. The similarities among batches are probably due because the raw material used comes from the same genetic line (black pigs).

The free fatty acids (FFA) detected in Sobrassada had different proportions than the obtained for the total fatty acid concentration (Table 3). The three batches only showed differences in the concentration of saturated free fatty acids. The batch S1 had a higher significant concentration of free saturated fatty acids than S2 and S3. However, there were not differences among batches in the content of free mono and polyunsaturated fatty acids. FFA was about 22-23% saturated, 61-62 monunsaturated and 16% polyunsaturated. The proportion of FFA in contrast to the total fatty acid composition was higher in polyunsaturated FFA and, in lower proportion, monounsaturated ones. This specific liberation of polyunsaturated FFA has been reported in fermented sausages (Zanardi et al., 2004; Marco et al., 2006) and in subcutaneous adipose tissue of dry-cured ham (Antequera et al., 1993). However, the FFA reported in sobrassada by Eim et al. (2008) were different from the ones

found in Sobrassada of Mallorca from black pig. Eim et al. (2008) detected higher contents of free mono and polyunsaturated fatty acids and probably, the reason is the different lean and fat tissues used as indicated Zanardi et al. (2004) when they compared different formulations of fermented sausages. The oxidation of unsaturated FFA will happen during the curing process and it is responsible of the generation of flavour compounds (Ordoñez et al., 1999).

<2>Aroma analysis

The extraction of volatile compounds from the headspace of Sobrassada of Mallorca from black pig using SPME indicated the presence of high number of volatile compounds (Figure 1). From all the compounds extracted, 84 were identified by mass spectrometry (Table 4). All of them have been previously detected in fermented sausages (Ansorena et al., 2001; Marco et al., 2006; Meynier et al., 1999; Stahnke, 1994) except 3 compounds; methyl nonanoate, 1-methyl-1H-pyrrole and 2-acetyl pyrrole. The chemical identification of these 3 compounds detected for first time in sobrassada was confirmed using authentic standards (Table 4).

The 84 compounds identified corresponded to different chemical classes, 13 esters (6-17% of the total extracted area), 13 aldehydes (0.6-1.1%), 13 alcohols (12-13%), 11 ketones (5-12%), 6 carboxylic acids (27-48%), 2 sulphur compounds (0.04-0.07%), 6 heterocyclic compounds (0.6-0.7%), 5 alyphatic hydrocarbons (1.2-1.8%), 5 aromatic hydrocarbons (8-31%), 8 compounds derived from spices (3-5%) and 2 antioxidant compounds (1.7-2.1%). The most abundant compounds were acetic acid (26-47%), toluene (7-29%), ethyl acetate (10-3.5%), 2,3-butanediol (3.5-5.5%), 1-propanol (1.5-3.8%), 2-heptanone (1.5-5.3%) and 2-nonanone (0.4-2.7%). However, the abundance of the volatile compounds is highly affected by the affinity of the fiber used, in this case the CAR/PDMS fibre. Therefore, these results can only be compared with those results obtained using the same extractions conditions. Therefore, studies on the aroma of fermented sausages using SPME and the same CAR/PDMS fibre (Marco et al., 2006; Flores et al., 2004; Marco et al., 2008) showed also a high abundance of acetic acid, 2,3-butanediol and ethyl acetate in fermented sausages. Moreover, these authors detected a high abundance of aldehydes in dry sausages that were higher than in sobrassada that only contained around 1% of the total extracted area. This low aldehyde proportion can be explained by the presence of antioxidants, BHT and BHA, in the sobrassada samples while the fermented sausages studied by Marco et al. (2006, 2008) and Flores et al. (2004), did not contain antioxidants and also they were manufactured without spices.

On the other hand, the abundance of compounds in the three sobrassada batches was very similar except for the batch S1. The S1 batch showed a lower abundance of ester compounds and acids while presented a high abundance of aromatic hydrocarbons, pyrazines and ketones. In particular, S1 contained higher significant abundance than the other batches of several compounds; toluene, benzene, 2, 6-dimethyl pyrazine, propyl benzene, 2-octanone and 2-nonanone while it contained lower abundances of acetic acid, ethyl propionate, propyl actetate, methyl butyrate and

other compounds (table 4). These differences in the content of volatile compounds could be related with the differences obtained in the content of moisture and free saturated fatty acids in S1 as indicated above.

In order to elucidate which compounds contribute to the aroma of sobrassada an olfactometry analysis was performed. Thirty five different aroma active zones were detected (figure 1, table 4), of them, thirty compounds were identified by matching mass spectra, linear retention indices and odour descriptions from references however, 5 of them were not identified. The identified odour active compounds belonged to different chemical classes; 7 were aldehydes, 4 esters, 4 alcohols, 4 carboxylic acids, 4 heterocyclic compounds, 3 ketones, 2 sulfur compounds and 2 terpenes. Many of these compounds were also detected as aroma active compounds in dry sausages (Schmidt and Berger, 1998a, b; Marco et al., 2007; Söllner and Schieberle, 2009). However, several of them have been identified for the first time as aroma active compounds in dry sausages; ethyl octanoate, 2-methyl-propanal, furfural, benzaldehyde, 1-propanol, 6-methyl-5-hepten-2-one, delta-hexalactone, tetramethyl-pyrazine, 1-methyl-1-H-pyrrole, acetyl-pyrrole, 3-carene and hexanoic acid although, this latest compound eluted together with α-terpinene.

The contribution of the compounds to the aroma of sobrassada can be evaluated by their detection frequency values (DF in table 4) that is the number of times that the volatile compound has been detected by the panelists. The highest DF value indicates a highest contribution of the volatile compound to the aroma of the product (Linssen et al., 1993; Pollien et al., 1997). The compounds that showed the highest DF values in sobrassada were ethyl 3-methylbutanoate, ethyl octanoate, furfural, benzaldehyde, (Z)-2-nonenal, 4-methyl-phenol, delta-hexalactone, acetic, 3-methyl-butanoic and heptanoic acids, 2-pentylfuran and 2-acetyl-pyrrole. In addition, 5 compounds contribute to the aroma with meaty notes such as ethyl octanoate, furfural, (Z)-2-nonenal, dimethyldisulfide and 1-methyl-1H-pyrrole.

This is the first time that the aroma active compounds of sobrassada have been identified. However, previous studies of aroma active compounds in dry sausages indicated that the most potent odourants were 3-methylbutanoic acid, ethyl butanoate, propyl 3-methyl butanoate, 2, 3-butanedione and acetic acid (Schmidt and Berger, 1998 a, b). Also, Marco et al. (2007) indicated the contribution of acetic acid, ethyl butanoate, 3-methylbutanoic acid and hexanal as potent odourants. Recently, Söllner and Schieberle (2009) elucidated the odour activity values (OAV) of aroma compounds in Hungarian salami. This odour-activity value (OAV) is a criterion for the selection of the most important aroma compounds in a food and they are calculated using the concentration and the odour threshold of the aroma compound (De Roos, 2007). Several compounds with highest OAV in hungarian salami (Söllner and Schieberle, 2009) were also detected in sobrassada such as acetic acid, acetaldehyde, methional, phenylacetaldehyde, 3-methyl butanoic acid and 4-methyl-phenol.

In 2009, Olivares et al. determined the contribution of volatile compounds to the aroma of dry fermented sausages processed without spices by calculating the OAV in oil and air. The compounds

with highest oil OAV were 2, 3-butanedione, ethyl 2-methyl butanoate, ethyl 3-methyl butanoate, hexanal and 3-methyl butanoic acid. However, the aroma perceived in the headspace was due to compounds with the highest air OAVs such as 3-methyl butanoic acid, ethyl 2-methyl butanoate, nonanal and octanal.

In summary, several compounds have been always detected as essential contributors to the aroma of dry sausages, 3-methyl butanoic acid, ethyl 3-methyl butanoate, 2, 3-butanedione and acetic acid. Moreover, the aroma of sobrassada of Mallorca from black pig was characterized by the presence of these volatile compounds and also other compounds such as ethyl octanoate, furfural, benzaldehyde, (Z)-2-nonenal, 4-methyl-phenol, delta-hexalactone, heptanoic acid, 2-pentylfuran and 2-acetyl-pyrrole which were responsible of specific aroma notes with high DF values.

The results suggest that the key aroma compounds were generated from the fermentation process (acetic acid and 2,3-butanedione), amino acid degradation products (3-methyl butanoic acid, ethyl 3-methyl butanoate, benzaldehyde), lipid autoxidation process (furfural, (Z)-2-nonenal, delta-hexalactone, heptanoic acid, 2-pentylfuran and 2-acetyl-pyrrole) and many other compounds from spices. In general, the contribution of the lipid autoxidation process to the aroma of sobrassada was important due to the presence of compounds not previously detected as key aroma compounds in dry sausages.

<1>CONCLUSION

Sobrassada of Mallorca from black pig was characterized by a fatty acid profile with a high content of monounsaturated fatty acids and by the generation during the curing process of polyunsaturated free fatty acids that were oxidized to generate flavour compounds. The key aroma compounds of sobrassada were identified and several of them have been always detected as essential contributors to the aroma of dry sausages, 3-methyl butanoic acid, ethyl 3-methyl butanoate, 2,3-butanedione and acetic acid. In addition, the aroma of sobrassada of Mallorca from black pig was due to the presence of another compounds such as ethyl octanoate, furfural, benzaldehyde, (Z)-2-nonenal, 4-methyl-phenol, delta-hexalactone, heptanoic acid, 2-pentylfuran and 2-acetyl-pyrrole which gave specific aroma notes.

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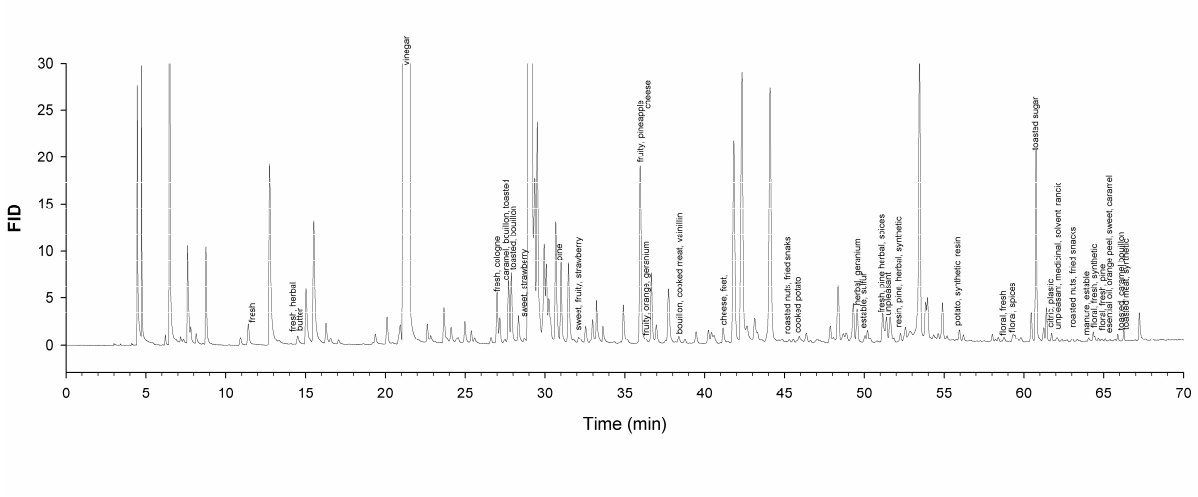
FID
Time (min)
vinegar
fresh
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cheese
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fresh, cologne
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roasted, bouillon
sweet, strawberry
pine
sweet, fruity, strawberry
fruity, orange, geranium
bouillon, cooked meat, vanillin
cheese, feet
roasted nuts, fried snacks
cooked potato
herbal, geranium
estérée, fruity
fresh, ripe herbal, spices
roasted nuts
resin, pine, herbal, synthetic
potato, synthetic, resin
floral, fresh
flora, spices
citric, plastic
medicinal, solvent rancid
roasted nuts, fried snacks
mineral, estérée
floral, fresh, synthetic
fruity, fresh, synthetic
essential oil, orange peel, sweet, caramel
roasted, caramel, bouillon
roasted, meat, synthetic

Figure 1.

Table 1. Proximate composition, water activity and pH in sobrassada of Mallorca from black pig dry cured sausage.

	Sobrassada samples			SEM[1]	p^2
	S1	S2	S3		
Moisture (%)	26.98 a	24.83 b	24.13 b	0.22	0.0002
Fat (%)	55.13	57.11	57.64	0.83	ns
Protein (%)	14.09	12.74	15.32	1.56	ns
pH	4.57	4.56	4.56	0.1	ns
a_w	0.843a	0.823b	0.814b	0.003	0.0153

[1]SEM: Standard error of the mean.

[2] *p* value denotes statistical significance among samples. Means followed by different letters are significant different; ns: non significant.

Table 2. Total Fatty acid composition in sobrassada of Mallorca from black pig dry cured sausages.

Fatty acids[1] (mg/100 g dw)	Sobrassada samples			SEM[2]	p[3]
	S1	S2	S3		
C14:0	351.2	350.4	336.8	5.24	0.2399
C16:0	5326.8	5261.2	4897.7	192.49	0.3640
C18:0	2337.8	2286.9	2042.4	90.10	0.1880
SFA	8015.8	7898.4	7276.9	285.26	0.2882
C16:1	903.9	930.8	879.0	29.09	0.5286
C18:1	11367.9	11408.2	10574.9	428.06	0.4129
C20:1 n9	210.6	214.9	180.6	10.33	0.1765
MUFA	12482.4	12553.9	11634.5	466.75	0.4139
C18:2 n6	1988.8	1939.4	1789.3	58.49	0.1829
C18:3 n3	179.8	191.1	164.4	10.11	0.3126
C20:2 n6	80.9	76.0	74.4	2.28	0.2611
C20:3 n6	15.8	18.1	17.3	3.05	0.8647
C20:4 n6	64.9	55.7	59.2	3.40	0.2982
C22:4 n6	13.6	14.3	12.7	0.51	0.2463
n6	2163.9	2103.5	1952.9	55.47	0.1491
C22:5 n3	34.7	42.0	30.3	4.01	0.2635
n3	214.5	233.1	194.8	10.23	0.1636
PUFA	2378.4	2336.6	2147.7	85.79	0.3045
Total	22876.6	22788.9	21059.0	814.94	0.3395

[1]SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; PUFA: polyunsaturated fatty acids.

[2]SEM: Standard error of the mean.

[3] p value denotes statistical significance among samples. Means followed by different letters are significant different.

Table 3. Free fatty acids concentrations in sobrassada of Mallorca from black pig dry cured sausages.

Fatty acids[1] (mg/100 g dm)	S1	S2	S3	SEM[2]	p[3]
C14:0	113.1	100.5	96.2	6.3	0.2855
C16:0	1406.0	1255.7	1303.2	38.3	0.1416
C18:0	360.5	304.5	342.4	42.8	0.6764
SFA	1879.6a	1660.6b	1741.8b	20.7	0.0111
C16:1	365.3	334.8	359.9	10.7	0.2480
C18:1	4580.2	4096.2	4422.8	184.7	0.3084
C20:1 n9	113.3	97.8	125.6	17.7	0.5963
MUFA	5058.8	4528.8	4908.3	212.9	0.3295
C18:2 n6	1079.4	968.4	1019.9	45.1	0.3500
C18:3 n3	107.0	105.2	109.1	4.3	0.8213
C20:2 n6	44.4	41.7	44.5	2.2	0.6279
C20:3 n6	12.6	11.6	12.2	0.7	0.5972
C20:4 n6	43.2	41.6	43.5	1.9	0.7824
C22:4 n6	6.9	7.2	8.0	0.4	0.2501
n6	1186.5	1070.5	1128.1	49.8	0.3804
C22:5 n3	17.6	17.7	18.5	1.0	0.8124
n3	124.6	122.9	127.6	5.1	0.8135
PUFA	1311.2	1193.4	1255.7	54.83	0.4246
Total	8249.6	7382.8	7905.8	262.1	0.2080

[1]SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; PUFA: polyunsaturated fatty acids.

[2]SEM: Standard error of the mean.

[3] p value denotes statistical significance among samples. Means followed by different letters are significant different.

Table 4. Volatile and aroma active compounds (expressed as percentage of the total area extracted by HS-SPME) identified in the headspace of sobrassada of Mallorca from black pig dry sausage.

N[1]	Compound (%)	MS LRI[2]	Sobrassada samples[3] S1	S2	S3	LRI GCO[4] Standard	LRI GCO[5]	GCO Descriptor	DF[6]	RI[7]
1	methyl acetate	549	1.37 b	3.29 a	2.90 a	549				y
2	2-methyl-propanal	590	0.04	0.02	0.04	591	602	fresh	2	x
3	hexane	598	0.03	0.03	0.03	600				y
4	1-propanol	610	1.52 c	2.90 b	3.76 a	614	628	fresh, herbal	2	x
5	2, 3 -butanedione	624	0.25	0.11	0.11	632	631	butter	3	x
6	2- butanone	629	0.81	1.07	0.92	638				y
7	ethyl acetate	634	3.48 c	10.81 a	7.69 b	643				y
8	2- butanol	642	0.38 b	2.37 a	1.81 a	654				y
9	benzene	675	0.05 a	0.02 b	0.01 b	682				y
10	2-methyl-1-propanol	680	0.07	0.09	0.04	683				y
11	3-methyl-butanal	688	0.11	0.03	0.18	691				y
12	heptane	701	0.14	0.17	0.18	700				y
13	2-methyl-butanal	700	0.06	0.04	0.05	699				y
14	acetic acid	716	26.25 b	47.58 a	46.26 a	702	701	vinegar	5	x
15	2-pentanone	732	1.61	0.62	0.48	730				y
16	pentanal	736	0.25	0.15	0.12	735				y
17	ethyl propionate	743	0.11 b	0.93 a	0.84 a	740				y
18	n-propyl acetate	748	0.29 b	1.57 a	1.82 a	744				y
19	methyl butyrate	754	0.07 b	0.13 a	0.12 a	751				y
20	unknown						766	fresh, cologne	2	
21	dimethyl disulfide	771	0.04	0.05	0.03	773	773	caramel, bouillon, toasted	2	x
22	3-hydroxy-2-butanone	778	1.63	1.07	0.89	778				y
23	1-methyl-1H-pyrrole	782	0.36	0.46	0.45	782	777	toasted, bouillon	2	x
24	unknown						785	sweet, strawberry	3	
25	toluene	788	29.15 a	6.92 b	11.29 b	789				y
26	3-methyl-1-butanol	793	0.33	0.50	0.42	789				y
27	octane	800	1.25	0.95	1.51	800				y
28	propanoic acid	808	0.51 a	0.05 b	0.05 b	802				y
29	1-pentanol	825	0.08	0.06	0.43	819	810	pine	2	x
30	ethyl butyrate	830	0.06	0.13	0.08	825	825	sweet, fruity, stawberry	3	x
31	2-hexanone	834	0.18	0.08	0.09	831				y
32	hexanal	839	0.24 a	0.09 b	0.09 b	836				y
33	butyl acetate	846	0.03 b	0.10 a	0.15 a	840				y
34	2-methyl-pyrazine	859	0.03a	0.02 b	0.02 b	858				y
35	ethyl 2-methyl-butanoate	877	0.01 b	0.04 a	0.02 b	872	871	fruit, pineapple	3	x
36	unknown						872	cheese	5	
37	ethyl 3-methylbutanoate	881	0.03 b	0.06 a	0.04 b	876	875	fruity, orange, geranium	5	x
38	2, 3-butanodiol	882	3.47	6.55	5.40	880				y
39	furfural	894	0.02	0.02	0.01	895	900	bouillon, cooked meat, vainillin	5	x
40	nonane	900	0.06	0.04	0.06	900				y
41	3-methyl-1-butanol acetate	905	0.04 b	0.09 a	0.06 b	904				y
42	1, 2-dimethyl-benzene	916	0.18 a	0.04 b	0.03 b	918				y
43	1-hexanol	922	0.14 a	0.11 a	0.05 b	917				y
44	2-heptanone	933	5.34 a	1.47 b	2.06 b	931				y
45	heptanal	940	0.05	0.04	0.04	936				y
46	3-methyl-butanoic acid	940	0.30	0.34	0.33	925	925	cheese, feet	5	x
47	α-pinene	941	0.13	0.14	0.14	945				y
48	2,6-dimethylpyrazine	943	0.14 a	0.03 b	0.04 b	944				y
49	2-heptanol	947	0.40	0.28	0.40	943				y

50	2-butoxy-etanol	952	5.77 a	0.30 b	0.32 b	953				y
51	unknown						963	roasted nuts, fried snacks	5	
52	3- (methylthio)-propanal	965	0.03	0.02	0.01	969	968	cooked potato	3	x
53	propyl-benzene	974	0.80 a	0.34 b	0.24 b					y
54	β-phellandrene	986	1.34	1.07	1.04					z
55	decane	1000	0.22 a	0.08 b	0.05 b	1000				y
56	β-myrcene	1002	0.24 a	0.12 b	0.12 b	1003	1002	herbal, geranium	4	x
57	2-pentyl-furan	1008	0.13	0.12	0.08	1010	1008	cowshed, sulfur	5	x
58	benzaldehyde	1013	0.13 a	0.05 b	0.04 b	1021	1021	fresh, pine, herbal, spices	5	x
59	1,2,4-trimethyl-benzene	1017	1.17	1.06	1.05					z
60	3-carene	1019	0.26	0.31	0.27	1027	1025	unpleasant	2	x
61	heptanol	1021	0.02	0.01	0.00					y
62	6-methyl-5-hepten-2-one	1031	0.09 a	0.05 b	0.03 b	1034	1032	resin, pine, herbal, synthetic	3	x
63	2-octanone	1035	0.19 a	0.06 b	0.06 b	1038				y
64	D-limonene	1042	1.80 a	0.98 b	0.96 b	1048				y
65	octanal	1044	0.02	0.02	0.02	1047				y
66	hexanoic acid + α-terpinene	1074	0.24	0.32	0.27	1065	1076	potato, synthetic, resin	4	x
67	benzeneacetadehyde	1104	0.17	0.12	0.13	1112	1110	floral, fresh	2	x
68	phenol	1109	0.03	0.02	0.02	1102				y
69	trans-2-octenal	1113	0.00	0.01	0.00	1117	1115	floral, spices	2	x
70	tetramethyl-pyrazine	1117	0.05	0.04	0.04	1120	1141	toasted sugar	3	x
71	2-nonanone	1139	2.65 a	0.41 b	0.94 b	1141				y
72	linalool	1148	0.06	0.05	0.05	1149				y
73	nonanal	1148	0.03	0.02	0.02	1151	1155	citric, plastic	2	x
74	methyl octanoate	1155	0.09	0.09	0.07	1156				y
75	2-acetyl pyrrole	1153	0.01	0.01	0.01	1156	1178	roasted nuts, fried snacks	5	x
76	heptanoic acid	1166	0.00	0.01	0.00	1162	1162	unpleasant, medicinal, solvent, rancid	5	x
77	4-methyl-phenol	1194	0.03	0.04	0.02	1190	1190	manure, cowshed	6	x
78	phenylethyl alcohol	1191	0.08	0.06	0.06	1195	1196	floral, fresh, synthetic	2	x
79	unknown						1206	floral, fresh, pine	5	
80	delta-hexalactona	1206	0.01	0.01	0.01	1215	1213	essential oil, orange peel, sweet, caramel	5	x
81	(Z)- 2-nonenal	1218	0.01	0.01	0.01	1222	1223	toasted caramel bouillon	6	x
82	4-terpineol	1226	0.05	0.03	0.03	1233				y
83	ethyl octanoate	1227	0.03	0.04	0.03	1226	1229	toasted meat synthetic.	6	x
84	methyl nonanoate	1258	0.01	0.01	0.01	1255				y
85	octanoic acid	1263	0.05	0.06	0.05	1253				y
86	2-undecanone	1345	0.02	0.00	0.01	1345				y
87	β-caryophyllene	1469	0.95 a	0.64 b	0.62 b	1480				y
88	butylated hydroxy toluene	1560	1.69	1.45	1.45					z
89	butylated hydroxyl anisole	1594	0.43	0.31	0.32					z

[1] Means followed by different letters are significant different ($p < 0.05$).

[2] Number of the aroma active zones in order of chromatographic elution.

[2]Linear retention indices (LRI) of the compounds eluted from the GC-MS using a DB-624 capillary column.

[3]Linear retention indices of the authentic standards injected in the GC-FID with the same column as above.

[4]Linear retention indices of the aroma detected in the sniffer port.

[5]DF: detection frequency value.

[6]R: Reliability of identification; x: identification by mass spectrum, coincidence with the LRI of an authentic standard and by coincidence with odour description (according to Burdock, 2002, and Acree and Arn, 2004); y: identification by mass spectrum and by coincidence with the LRI of an authentic standard, z: tentatively identified by mass spectrum.