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Volatile Compounds Present in Traditional Meat Products (charqui and longaniza sausage) in Chile

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ABSTRACT

The aim of this work was to identify and quantify the volatile compounds in five different commercial brands of charqui and longaniza sausages. Volatile compounds were extracted from some samples headspace using solid phase microextraction (SPME). The identification and quantification were made through the gas chromatography with a mass-selective detector (GS-MS). Fifty-four volatile compounds were identified in charqui samples and thirty-two volatile compounds in longaniza sausages. The chemical groups of the volatile compounds found in both the products were: aldehydes, alcohols, ketones, organic acids, furans, aromatic and aliphatic hydrocarbons. Significant differences were found ($p<0.05$) in the volatile compounds among the brands of longaniza and charqui. A characteristic volatile compounds profile was not found in the analyzed products. However, an important percentage of the volatile compounds in charqui came from the lipid oxidation. In the case of longanizas sausages, volatile compounds come mainly from the carbohydrates fermentation and spices.

Key words: SPME, volatile compounds, sausage, charqui

INTRODUCTION

The traditional meat products such as longaniza sausages and charqui have some particular sensorial characteristics. Aroma is determining the product acceptance.

In this sense, fat plays a preponderant role in the sensorial properties of meat products as it acts as volatile compounds precursor and also as aroma compounds solvent (Olivares et al. 2009a). On the other hand, protein degradation leads to the formation of aromatic compounds (Stahnke 2002). Besides, proteins have an effect on the flavor and aroma perception because the structure interacts with the flavor components, which affect the concentration of volatile compounds in the headspace (Gianelli et al. 2003; Pérez-Juan et al. 2008). In this aspect, Olivares et al. (2009b) have reported that the intramuscular fat and protein fraction are the tissues that mostly contribute to develop the flavour in dry fermented sausages. Also, the microbial growth in the sausages is responsible for developing an important number of volatile compounds (Stahnke 2002).

Charqui is a dry salty meat product, usually elaborated with the horse or bovine meat. Curing process results in a low water activity product, between 0.7 to 0.75 (Pinto et al. 2002; Youssef et al. 2003). Elaboration process permits the chemical and biochemical reactions, which are responsible for the flavor (Martin et al. 2009).

Charqui is the result of the use of hurdle technology to inhibit the micro-organisms growing; these barriers are sequentially applied, salt, sodium nitrate, dehydration (Youssef et al. 2003). Longaniza sausages are elaborated with

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pork, pork back fat, additives and spices. Chilean Food Sanitary Regulations (RSA 2003) define this product as a fresh raw meat product as its processing does not results significant variations in the Aw and pH compared to the fresh meat.
Solid phase microextraction (SPME) is used to detect the volatile compounds present in dry fermented sausages (Marco et al. 2007; Gianelli et al. 2009; Olivares et al. 2009b) and cured products (Gianelli et al. 2002; Ventanas et al. 2008). The effect of animal species over the volatile compounds in the dried meats has been studied (Hierro et al. 2004). It is necessary to point out here that there is no clear regulation for the elaboration of the parameters and final characteristics of the Chilean traditional meat products. There is a wide variety of ingredients, processing and proportions among the producers. The purpose of this investigation was to study the volatile compounds present in the headspace of different traditional brands of charqui and longaniza sausages using the SPME technique.

MATERIALS AND METHODS

Samples

Charqui

Five different traditionally elaborated charqui brands were bought from the local market. Elaboration process consisted in the use of lean horse meat which was salted and dried in a convective oven at 60º. All the samples were vacuum stored at -20ºC until the analysis.

Longaniza sausages

Five different traditionally elaborated longaniza sausages brands were bought from the local market. The samples were elaborated with pork, pork back fat, additives and spices, such as the salt, oregano (*Origanum vulgare*), paprika (*Capsicum annuum L. var longum*), chilli pepper (*Capsicum annuum L. var grossum*) and garlic (*Allium sativum L.*), minced and mixed together, finally stuffed into a casing and smoked. All the samples were vacuum stored at -20ºC until analyzed.

Volatile compounds extraction

The headspace volatile compounds extraction was made by using the SPME Carboxen/ Polidemethyl-siloxane (CAR / PDMS) fibre of 85 µm, supplied by the Supelco (Bellafonte, PA, USA). Before each analysis, the fibres were preconditioned in the injection port of the gas chromatograph as indicated by the manufacturer. The samples were cut into 4 mm cubes, a 3 g sample was introduced into a vial closed with a twisted-off lid and sealed with the PTFE silicone septum (Supelco, Bellafonte, PA. USA). The samples were heated in a thermo block (Equilab 2050-ICE, Paris, France) for 90 min at 30ºC, with the purpose of equilibrating the headspace. The SPME fiber was exposed to the vial headspace for 30 min at 30ºC and the adsorbed compounds were quantified and identified through the gas chromatography analysis with a mass detector (GC-MS). All the samples were analysed in triplicate for each product brand.

Identification and quantification of volatile compounds

The volatile compounds adsorbed by the fibre were desorbed in the injection port of the Shimadzu GC, series GC-17-A, equipped with a Shimadzu GCMS QP5050A mass-selective detector (Kyoto, Japan). Desorption was performed by keeping the fibre in the injection port for 5 min at 220°C with the purge valve off (splitless mode). The compounds were separated in a DB-624 capillary column of 60 m long, 0.25 mm id and film thickness 1.8µm (J&W Scientific, Falson, USA). Helium was used as the carrier gas at a linear velocity of 28.3 cm s^{-1}. The temperature program began when the fibre was inserted, the temperature was held at 38°C for 8 min, ramped to 150°C at 8°C min^{-1}, then to 220ºC at 10°C min^{-1} and held at 220°C for 21 min, giving a total run time of 50 min. The GC-MS interface was maintained at 240°C. Mass spectra were obtained by electron impact at 70 eV. Mass spectra data of volatile compounds were acquired in the range 25-400 amu.
The volatile compounds were identified by comparison with mass spectra from the collection base (Nist' 107 and Nist' 21). The identification was confirmed by the injection of standard compounds when available and using the Kovats retention index (KI) reported in the bibliography.

Statistic analysis

Results were expressed as the mean of the total ions area of each volatile compound. The samples were analyzed in triplicate using the variance analysis (ANOVA), employing the statistics software Statgraphics Plus 5.1. Significant effects

were compared through the Fisher less significant differences test (LSD).

RESULTS AND DISCUSSION

The volatile compounds absorbed by the SPME fibre were identified and quantified through the gas chromatography with a selective-mass detector. (Table 1, Table 2). In charqui, aldehydes and alcohols presented higher area percentages.
Aldehydes were found in the highest proportion in three of the five samples, with an area percentage that varied between 54.28-66.14%; in the other two samples, the area percentage was 17.09 and 7.98%. Alcohols percentage varied between 6.89-14.88%.
In longaniza sausages, the highest proportion of the volatiles compounds was sulphur compounds and organic acids. The highest proportion of sulphur compounds found in three of the analyzed samples varied between 21.5-37.2%. In the other samples, the highest percentage corresponded to carboxylic acids, 65.1 and 38.4%.

Table 1 - Volatile compound identified and quantified in headspace of charqui

No[A]	COMPOUND	KI[B]	RI[C]	Origin	SAMPLE 1		SAMPLE 2		SAMPLE 3		SAMPLE 4		SAMPLE 5	
					area[E]	%[F]	area[E]	%[F]	area[E]	%[F]	area[E]	%[F]	area[E]	%[F]
	ALCOHOLS													
1	Etanol	508	a	CA[1,4,5]	-	-	-	-	-	-	5016979	1.06	-	-
12	1-Penten-3-ol	734	a	LO[1,2,3,4,7]	6758491[a]	1.48	5783656[ab]	1.07	5405919[ab]	1.05	4327696[b]	1.00	1687715[c]	0.28
17	3-Methyl-1-butanol	785	b	AA[1,2,3,4]	-	-	-	-	-	-	-	-	2212232	0.37
21	1-Pentanol	812	c	LO[1,3,4]	11137321[b]	2.45	8854092[c]	2.60	16358930[a]	3.19	7118032[c]	1.64	3896855[d]	0.65
22	2-Penten-1-ol	822	c	LO[7]	2777164[a]	0.61	-	-	2808574[a]	0.55	2404023[a]	0.55	-	-
26	2,3-Butanediol	860	b	CA[4]	2235535[a]	0.49	-	-	-	-	-	-	33600970[b]	5.59
27	2-Heptanol	868	b	LO[1]	10069622	2.21	-	-	-	-	-	-	-	-
33	1-Hexanol	918	a	LO[1,3,4,]	-	-	1727859[a]	0.51	2008673[a]	0.39	-	-	-	-
42	1-Heptanol	999	c	--	3209286[c]	0.70	2305266[d]	0.68	5692498[a]	1.11	3852547[b]	0.89	-	-
49	1-Octen-3-ol	1026	b	β[3,4]/LO[2,7]	16482168[b]	3.62	22102424[a]	6.49	16848308[b]	3.28	16485745[b]	3.80	-	-
59	1-Octanol	1117	a	LO[1,3,4]	-	-	2370631[b]	0.70	5227057[a]	1.02	2532829[b]	0.58	-	-
61	2-Octen-1-ol, (Z)	1121	c	--	-	-	7548616[a]	2.22	8630066[a]	1.68	4481351[b]	1.03	-	-
	Total Alcohols				*52669587*	*11.56*	*50692544*	*14.88*	*62980025*	*12.28*	*46219202*	*10.65*	*41397772*	*6.89*
	ALDEHYDES													
2	Propanal	523	b	LO[2,3]	-	-	-	-	-	-	35506653	8.18	-	-
5	Butanal	629	b	LO[3,4]	-	-	-	-	2002632	0.39	-	-	-	-
9	2-Methyl butanal	700	a	AA[1,3,4,5]	7337411[a]	1.61	254464[b]	0.07	3049138[b]	0.59	-	-	-	-
13	Pentanal	737	a	LO[1,3,4,7]	15850434b	3.48	5409125[c]	1.59	24127057[a]	4.70	14068149[b]	3.24	3434782[c]	0.57
18	2-Methyl-2-butenal	787	c	-	5359113[a]	1.18	2034704[b]	0.60	5941091[a]	1.16	5038758[a]	1.16	-	-
23	Hexanal	837	a	LO[1,2,3,4,5,7]	124535491[b]	27.37	35820286[c]	10.51	196769491[a]	38.36	148290143[b]	34.18	42187894[c]	7.02
28	2-Methyl-2-pentenal	873	c	-	-	-	-	-	6465800[a]	1.26	4089554[b]	0.94	-	-
38	Heptanal	946	a	LO[1,2,3,4,5,7]	12082020[b]	2.65	5802476[c]	1.70	18630426[a]	3.63	18070573[a]	4.16	2293877[d]	0.38
51	Octanal	1050	b	LO[1,2,3,4,5]	9381183[b]	2.06	-	-	11859768[ab]	2.31	16822116[a]	3.88	-	-
56	2-Methyl-2-heptenal	1091	c	-	-	-	1867552[b]	0.55	4756974[a]	0.93	2198109[b]	0.51	-	-
66	Nonanal	1147	b	LO[1,2,3,4,5,7]	8980093[c]	1.97	7030854[c]	2.06	20712533[b]	4.04	33248456[a]	7.66	-	-
73	2-Nonenal	1183	c	LO[2,3,4]	10623526[a]	2.33	-	-	18083536[b]	3.53	9656020[b]	2.23	-	-
	Total Aldehydes				*194149271*	*54.28*	*58219461*	*17.09*	*312398446*	*60.90*	*286988531*	*66.14*	*47916553*	*7.98*
	ACIDS													
8	Acetic acid	698	a	CA[1,3,4,5]	97753380[b]	21.46	1178622221[b]	34.59	27005016[c]	5.26	27362249[c]	6.31	346600243[a]	57.69
21	Propanoic acid	793	a	LO[3,4]	4930536[b]	1.08	15473310c	4.54	10450346[a]	2.04	11906859[c]	2.74	6291695[d]	1.05
25	Butanoic acid	860	b	CA[4,5]	3297701[b]	0.72	13077448[a]	3.84	2593611b	0.51	2409590[b]	0.56	2218807[b]	0.37
32	3-Methyl butanoic acid	911	b	AA[1,2,4]	-	-	-	-	-	-	-	-	7161035	1.19
52	Hexanoic acid	1052	b	LO[3,4]	4780124[b]	1.05	-	-	11976141b	2.33	8890856[ab]	2.05	-	-
	Total Acids				*110761741*	*24.32*	*146412979*	*42.97*	*52025114*	*10.14*	*50569554*	*11.65*	*362271780*	*60.30*

(cont. table 1)

(cont. table 1)

No[A]	COMPOUND	KI[B]	RI[C]	Origin[D]	SAMPLE 1		SAMPLE 2		SAMPLE 3		SAMPLE 4		SAMPLE 5	
					area[E]	%[F]	area[E]	%[F]	area[E]	%[F]	area[E]	%[F]	area[E]	%[F]
	KETONES													
3	Acetone	529	b	CA[3,4]	-	-	-	-	-	-	10566684	2.44	-	-
6	2,3-Butanedione	636	a	CA[1,4,5]	-	-	-	-	-	-	-	-	34086004	5.67
7	2-Butanone	640	a	CA[1,2,3,4]	7832215[a]	1.72	5212651[b]	1.53	5036991bc	0.98	3758203[c]	0.87	4209842[bc]	0.70
14	2,3-Pentanedione	738	b	B[3,4]	3747011[a]	0.82	-	-	-	-	2205447[a]	0.51	3785400[a]	0.63
16	3-Hydroxy-2-butanone	777	b	CA[1,4,5]	2934003[b]	0.64	-	-	-	-	-	-	47400648[a]	7.89
35	2-Heptanone	938	b	B[3,4]/LO[5,7]	-	-	7286484[b]	2.14	9740527[a]	1.90	4673685[c]	1.08	3206078[d]	0.53
64	2-Tridecanone	1138	c	--	-	-	3546082	1.04	-	-	-	-	-	-
70	3,5-Octadien-2-one	1158	c	LO[7]	-	-	-	-	-	-	5186012[a]	1.20	2157680[b]	0.36
	Total Ketones				*14513229*	*3.19*	*16045217*	*4.71*	*14777518*	*2.88*	*26390031*	*6.08*	*94845652*	*15.79*
	ALIPHATIC HYDROCARBONS													
43	Decane	1000	a	LO[1,3,4]	-	-	1770182	0.52	-	-	-	-	-	-
55	2,8-Dimethyl undecane	1060	c	--	3935898	0.86	-	-	-	-	-	-	-	-
74	Dodecane	1110	a	LO[3,4]	-	-	-	-	8309037	1.62	-	-	-	-
71	2,5-Dimethyl undecane	1163	c	--	2255626	0.50	-	-	-	-	-	-	-	-
75	Tridecane	1300	a	S[9]	2189631b	0.48	9174681[a]	2.69	1918385[b]	0.37	2398664[b]	0.55	1617970[b]	0.27
76	Tetradecane	1400	a	S[9]	2560792c	0.56	4831790[a]	1.42	2247420[c]	0.44	3451722[b]	0.80	2363748[c]	0.39
	Total Aliphatic Hydrocarbons				*10941947*	*2.40*	*15776653*	*4.63*	*12474842*	*2.43*	*5850386*	*1.35*	*3981718*	*0.66*
	AROMATIC HYDROCARBONS													
19	Toluene	789	b	SK[1]/AA[4]	3411555[ab]	0.75	-	-	2596068[ab]	0.51	3594210[a]	0.83	2494260[b]	0.42
29	1,3-Dimethyl benzene	873	c	--	-	-	-	-	-	-	2748829	0.63	-	-
30	Ethylbenzene	881	c	SK[1]	-	-	-	-	-	-	1871494	0.43	-	-
	Total Aromatic Hydrocarbons				*3411555*	*0.75*	-	-	*2596068*	*0.51*	*8214533*	*1.89*	*2494260*	*0.42*
	PYRAZINES													
36	2,6-Dimethylpyrazine	945	b	SK[1]	-	-	2541359[a]	0.75	-	-	-	-	1936976[b]	0.32
39	2,3-Dimethylpyrazine	949	c	LO[7]	2890969b	0.63	-	-	-	-	-	-	6391996[a]	1.06
62	Tetramethylpyrazine	1121	c	SK[1]	8873882c	1.95	2724211b	0.80	-	-	-	-	33226985[a]	5.53
68	3,5-Diethyl-2-methylpyrazine	1155	c	--	-	-	-	-	-	-	-	-	3872333	0.64
	Total Pyrazines				*11764851*	*2.58*	*5265570*	*1.55*	-	-	-	-	*45428290*	*7.56*
	FURANS													
10	2-Ethylfuran	718	b	LO[1,4]	3935932	0.86	-	-	-	-	-	-	-	-
46	2-PentylFuran	1012	b	LO[1,4,5,7]	8939128b	1.96	1838388c	0.54	13334149[a]	2.60	7726375[b]	1.78	2448114[c]	0.41
48	Butyrolactone	1019	b	LO[4]	44365619[a]	9.74	43848158[a]	12.87	38406269[b]	7.49				
72	5-heptyldihydro2 (3H)-Furanone (γ undecalactone)	1171	c	--	-	-	2631911ab	0.77	3981028[a]	0.78	1954409[b]	0.45	-	-
	Total Furans				*57240679*	*12.57*	*48318457*	*14.18*	*55721446*	*10.86*	*9680784*	*2.23*	*2448114*	*0.41*

[A] Number of peak as in figure 1 and 2. [B] Kovats index calculate for DB-624 capillary column (J& W Scientific; 60 m, 0.32mm i.d. 1.8 μm). [C] Reliability of identification: a, mass spectrum and retention time identical with an authentic sample, b mass and Kovats index from literature in agreement; c, tentative identification by mass spectrum. [D] Main Chemical/biochemical origin: LO, lipid oxidation; AA, amino acid catabolism; CA carbohydrate fermentation; β, lipid β-oxidation; SK, smoke; S, spices and condiment . Origin has been reported in has been reported in (1) Hierro et al. (2004), (2) Théron et al. (2010), (3) Flores and Olivares (2008), (4) Marco et al. (2008), (5) de Campos et al. (2007), (6) Guillen and Manzanos (1999), (7) Aaslyng and Schäfer (2008), (8) Calvo-Gómez et al. (2004), (9) Kocsis et al. (2002). [E] Results expressed as the mean of three replicates of total ion current (TIC) area of GC/MS. a, b, c, d values in the same row with different letters are significantly different ($p<0.05$), - no detected. [F] Percentage of total TIC area.

Table 2 - Volatile compound identified and quantified in headspace of longaniza sausage.

No[A]	COMPOUND	KI[B]	RI[C]		Origin[D]	SAMPLE 1		SAMPLE 2		SAMPLE 3		SAMPLE 4		SAMPLE 5	
						area[E]	%[F]	area[E]	%[F]	area[E]	%[F]	area[E]	%[F]	area[E]	%[F]
	ALCOHOLS														
1	Etanol	508	a		CA [1,2,5]	43280003[d]	3.66	127711363[b]	7.76	71951573[c]	5.66	7940830[d]	2.03	224045995[a]	29.26
17	3-Methyl-1-butanol	785	b		AA [1,2,4,3]	-	-	8235638	0.5	-	-	-	-	-	-
34	2-Furanmethanol	936	a		--	-	-	-	-	46147966[b]	3.63	16442970[c]	4.2	63482097[a]	8.29
37	2-Butoxyethanol	946	b		--	-	-	35795396[a]	2.17	32154408[a]	2.53	-	-	-	-
63	Linalool	1117	c		S [9,10,11]	10257899a	0.87	10998146[a]	0.67	-	-	-	-	-	-
	Total Alcohols					*10257899*	*4.53*	*182740543*	*11.1*	*150253947*	*11.82*	*24383800*	*6.23*	*287528092*	*37.55*
	ALDEHYDES														
23	Hexanal	837	a		LO[1,2,3,4,5]	198309427[a]	16.79	26316692[b]	1.6	-	-	-	-	-	-
	Total Aldehydes					*19830942[a]*	*16.79*	*26316692[b]*	*1.6*						
	ACIDS														
8	Acetic acid	698	a		CA [1,3,4,5]	230337468[bc]	19.5	174396482[c]	10.59	653175761[a]	51.38	42764298[d]	10.93	282747975[b]	36.92
20	Propanoic acid	790	a		LO [3]	-	-	-	-	164740838[a]	12.96	-	-	7900592[bc]	1.03
25	Butanoic acid	860	b		CA [4,5]	-	-	10789201[a]	0.66	9607102[a]	0.76	-	-	3182858	0.42
	Total Acids					*230337468*	*19.5*	*185185683*	*11.25*	*827523701*	*65.1*	*42764298*	*10.93*	*293831425*	*38.37*
	KETONES														
6	2,3-Butanedione	636	a		CA [1,2,5]	-	-	48187486[a]	2.93	18776141[b]	1.48	-	-	-	-
7	2-butanone	640	a		CA [1,3,4,5]	-	-	-	-	25462928	2	-	-	-	-
15	1-Hidroxy-2-propanone	739	c		CA [1]	-	-	9322478	0.57	-	-	-	-	-	-
16	3-Hydroxy-2-butanone	777	b		CA [1,4,5]	9000630[d]	0.76	151072886[a]	9.18	13226864[cd]	1.04	22005407[bc]	5.62	21919760[bc]	2.86
24	1- Hydroxy-2-butanone	843	c		--	-	-	-	-	-	-	6348606	1.62	-	-
40	2-Methyl-2-cyclopenten-1-one	977	c		SK[1,6]	-	-	-	-	-	-	5482497[a]	1.4	3261698[b]	0.43
	Total Ketones					*9000630*	*0.76*	*208582850*	*12.68*	*57465933*	*4.52*	*33836510*	*8.64*	*25181458*	*3.29*
	SULPHUR COMPOUNDS														
4	Allyl mercaptan	617	c		S [8]	288221238[a]	24.4	54496031[b]	3.31	101302461[b]	7.97	128939201[b]	32.95	74950565[bc]	9.79
11	Allyl methyl sulphide	720	a		S[5,8]	12127915[b]	1.03	62824235[a]	3.82	5872116[b]	0.46	16542669[b]	4.23	4332927[b]	0.57
31	Allyl sulphide	891	a		S [8]	16712415[a]	1.41	17243721[a]	1.05	-	-	-	-	-	-
65	Diallyl disulphide	1141	c		S [8]	90377527[b]	7.65	219434304[a]	13.33	-	-	-	-	13998343[c]	1.83
	Total Sulphur Compounds					*407439095*	*34.49*	*353998291*	*21.51*	*107174577*	*8.43*	*145481870*	*37.18*	*93281835*	*12.19*
	TERPENES														
45	β- Myrcene	1006	c		S [5,9,10]	7253396[a]	0.61	8732708[a]	0.53	6083554[a]	0.48	6315672[a]	1.61	2386165[a]	0.31
46	β-Pinene	1009	b		S [10,11]	35008873[ab]	2.96	69811412[a]	4.24	12116131[b]	0.95	8553241[b]	2.19	-	-
50	D-Limonene	1020	c		S [5,9,10]	-	-	9721402	0.59	-	-	-	-	-	-
54	p-Cymene	1058	c		S [10,11]	85595749[b]	7.25	300922162[a]	18.28	14469152[c]	1.14	13659908[c]	3.49	5047566[c]	0.66
67	α-Terpineol	1142	c		S [10,11]	40988839[a]	3.47	45325361[a]	2.75	-	-	-	-	-	-
	Total Terpenes					*168846857*	*14.29*	*434513045*	*26.39*	*32668837*	*2.57*	*28528821*	*7.29*	*7433731*	*0.97*
	HYDROCARBONS														
47	1-Methoxycyclohexane	1013	c		SK	-	-	-	-	5495876[a]	0.43	-	-	5227005[a]	0.68
57	Undecane	1100	a		LO [1,3]	6499981[a]	0.55	9838441[a]	0.6	-	-	-	-	-	-
58	1,3-Dimethyl-2-cyclopentanediene	1113	c		--	-	-	-	-	7475180[b]	0.59	10875044[a]	2.78	-	-
	Total Hydrocarbons					*6499981*	*0.55*	*9838441*	*0.6*	*12971056*	*1.02*	*10875044*	*2.78*	*5227005*	*0.68*
	PHENOLS														
60	Phenol	1104	a		AA[3]/SK[1]	5880963[c]	0.5	10514984[b]	0.64	15910159[a]	1.25	16077311[a]	4.11	11222148[b]	1.47
69	2-Methoxyphenol (guaicol)	1145	c		SK [1,6]	-	-	-	-	31917306[a]	2.51	25018471[ab]	6.39	19373125[b]	2.53
	Total Phenols					*5880963*	*0.5*	*10514984*	*0.64*	*47827465*	*3.76*	*41095782*	*10.5*	*30595273*	*4*

(cont. table 2)

(cont. table 2)

No[A]	COMPOUND	KI[B]	RI[C]	Origin[D]	SAMPLE 1		SAMPLE 2		SAMPLE 3		SAMPLE 4		SAMPLE 5	
					area[E]	%[F]	area[E]	%[F]	area[E]	%[F]	area[E]	%[F]	area[E]	%[F]
	FURANS													
41	1-(2-Furanyl)-ethanone	985	c	SK [6]									7729795	1.01
48	Butyrolactone	1019	b	LO [4]	-	-	10085924[ab]	0.61	11331786[a]	0.89	11674234[a]	2.98	6750948[b]	0.88
53	2(5H)-Furanone	1036	c	SK [6]	-	-	-	-	6437829[b]	0.51	5695000[b]	1.46	8223704[a]	1.07
	Total Furans				-	-	*10085924*	*0.61*	*17769615*	*1.40*	*17369234*	*4.44*	*22704447*	*2.96*

[A] Number of peak as in figure 1 and 2. [B] Kovats index calculate for DB-624 capillary column (J& W Scientific; 60 m, 0.32mm i.d. 1.8 μm). [C] Reliability of identification: a, mass spectrum and retention time identical with an authentic sample, b mass and Kovats index from literature in agreement; c, tentative identification by mass spectrum. [D] Main Chemical/biochemical origin: LO, lipid oxidation; AA, amino acid catabolism; CA carbohydrate fermentation; β, lipid β-oxidation; SK, smoke; S, spices and condiment . Origin has been reported in has been reported in (1) Hierro et al. (2004), (2) Théron et al. (2010), (3) Flores and Olivares (2008), (4) Marco et al. (2008), (5) de Campos et al. (2007), (6) Guillen and Manzanos (1999), (7) Aaslyng and Schäfer (2008), (8) Calvo-Gómez et al. (2004), (9) Kocsis et al. (2002), 10 Baranauskiene et al. (2006), Jerkovic et al. (2001). [E] Results expressed as the mean of three replicates of total ion current (TIC) area of GC/MS. a, b, c, d values in the same row with different letters are significantly different ($p<0.05$), - no detected. [F] Percentage of total TIC area.

Charqui

Fifty-four different volatile compounds were extracted from the charqui sample headspace (Table 1). Most volatile compounds extracted showed statistically significant differences concerning the area. This indicated a high volatile variability among the charqui brands. Some volatile compounds appeared only in one or two samples. Figure 1 shows a characteristic chromatogram of charqui. Groups with the highest amount of the volatile compounds and areas were aldehydes and alcohols, each group with twelve different compounds.

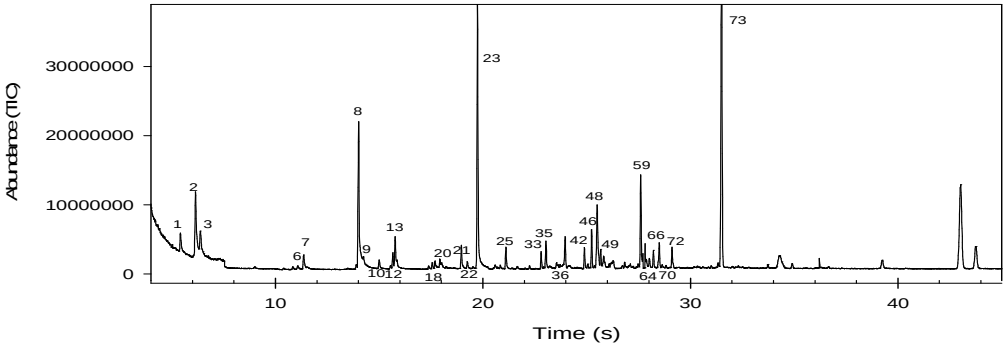

Figure 1 - Chromatogram obtained by SPME after exposition for 0.5 h at 30°C in the headspace of charqui.

The area percentage corresponding to those compounds generated by the lipid oxidation varied between 39.83-79.20% in four of the five analyzed samples. This could eventually demonstrate that the oxidation reactions have a relevant role in the aroma of the product. Results showed a linear correlation (r^2= 0.94) between the lipids content in the charqui samples (except sample 4) and the response area of the total volatile compounds coming from the lipid oxidation. It was also possible to correlate in a linear way (r^2= 0.91) the lipid content of charqui samples (except sample 4) with the total response area of volatiles compounds found in each sample. Both the correlations were inversely proportional, that is to say, as the lipid content increased in the charqui sample, the response area of volatile compounds present in the headspace decreased. Lipids are excellent solvents and also decrease the vapour pressure of a large number of volatiles compounds; therefore, a higher amount of lipids decreases the volatile compounds content in the headspace. Twenty-three volatile compounds were generated as a consequence of lipid oxidation and most of them were mainly aldehydes and alcohols. Linear aldehydes: pentanal, hexanal and heptanal

were found in all the samples. Linear aldehydes may be formed by autoxidation of some unsaturated fatty acids (Stahnke 2002). Linear aldehydes, pentanal, hexanal, heptanal, octanal and nonanal were also previously identified by Hierro et al. (2004) in the headspace of dried and salted horse meat. Of the aldehydes group, hexanal was the compound with the highest area percentage in four of the analyzed samples.

All the alcohols produced by the lipid oxidation 1-pentanol, 1-peten-3-ol, 1-octanol, and 1-hexanol had been previously reported as present in horse meat charqui samples by Hierro et al. (2004) and in the cured ham by Gianelli et al. (2002). Among these alcohols produced by the oxidative decomposition, 5.59% of 2,3-butanediol was found in only one of the samples and in the rest of the samples, the most abundant was 1-pentanol that was produced by lipid oxidation and was present in all the analyzed samples. However, the area percentage of each of these compounds did not reach higher than 3.2%. 1-octen-3-ol produced by beta oxidation (Flores et al. 2008) reached 6.49% in one of the analyzed samples but in the rest of the samples, only reached as high as 3.28 to 3.80%. On the other hand, 2-peten-1-ol was identified as a product of the lipid degradation in pork meat with an addition of linoleic acid and its odor descriptor was chemical, synthetic (Aaslyng and Schäfer 2008).

It was possible to identify only two ketones, 2-heptanone and 2,3-pentadione provided by the beta oxidative degradation in charqui. 2-heptanone was identified in four samples; this ketone has been reported as present in cured products (Yu et al. 2008) and in cooked beef meats (Machiels and Istasse 2003). The area percentage of each ketone was not higher than 1.04%. Aaslyng and Schäfer (2008) detected 3,5-octadien-2-one in cooked pork meat after the addition of α-linolenic acid. However, α-linolenic acid compound of the cured intramuscular horse fat only reached 4,5% (Paleari et al. 2003).

In relation to hydrocarbons, tridecane and tetradecane were identified as present in all the charqui samples. However, their percentage was not higher than 2.69% for tridecane and 1.42% for tetradecane. These compounds had been previously reported in the meat products (Clakin and Hodgen 2007). Besides, the presence of decane has been reported in charqui samples (Hierro et al. 2004) and in the cured products (Gianelli et al. 2002). Straight chained aliphatic hydrocarbons with less than 10 carbon atoms arising mainly from the lipid oxidation (Muriel et al. 2004). On the other hand, Tejeda et al. (2001) reported that long chained aliphatic hydrocarbons could be accumulated in the fat deposits of the animal probably from the feeding. Compounds, whose origin is the bacterial metabolism, specifically carbohydrates fermentation, represented an area percentage lower to 39.96% in four of the five analyzed samples. Sample 5 presented a percentage of 77.92% for those compounds coming from the carbohydrates fermentation; the same sample showed the lowest area percentage (11.78%) of all the volatile compounds produced by the lipid oxidation. The highest percentage of the compounds originated by the fermentation and a comparatively low percentage of compounds originated by the oxidation demonstrated that in this particular sample, there was a higher degree of bacterial metabolism. Pinto et al. (2002) found the evidence leading to the conclusion that the elaboration of jerked beef, therefore charqui, was a fermentation process.

Four furans compounds were found in the charqui samples. The presence of these compounds in the food has been related to the heating processes, smoke and Maillard reaction (Yu et al. 2008). 2-pentyl-furan was identified in five charqui samples and its area percentage varied between 2.6 and 0.41%.

In the pyrazine family, only one of the analyzed samples reached a percentage of 7.56%, and tetramethylpyrazine was the compound that showed the highest area percentage. It appeared after the smoking process (Hierro et al. 2004). However, 2,6-dimethylpyrazine and tetramethyl pyrazine were identified as odour-active in the cured ham. These compounds were probably formed by the Maillard reaction (Théron et al. 2010). Besides, 2,5-dimetylpyrazine and 2,3-dimetylpyrazine were described by Aaslyng and Schäfer (2008) as present in the cooked minced meat with the addition of fatty acids, but in general, pyrazine formation was not under the influence of fatty acids.

The area percentages among all the samples showed statistically significant differences. Those differences could be related to the conditions of the elaboration process and the raw material used for the manufacture of these products.

Longaniza sausages

Thirty-two volatile compounds were extracted from the samples headspace. Figure 2 shows a characteristic chromatogram of longaniza sausage. Most of volatile compounds have been previously detected (Marco et al. 2008; Gianelli et al. 2009), except for those compounds provided by the spices and the smoking process. All the sulphur compounds that were identified in the samples came from garlic (Calvo-Gómez et al. 2004). Three of the analyzed samples showed a percentage of sulphur compounds that varied between 21.51 and 37.18%: However, in those samples, where this percentage was lower, 8.43 and 12.19%, the percentage of volatile compounds resulting from the fermentation reached 61.56 and 69.04%. The antimicrobial properties of the active compounds in garlic have been demonstrated (Kim et al. 2010). The presence of higher percentage of garlic volatile compounds showed that this product in particular was formulated with higher amounts of garlic, and therefore it might have a higher antimicrobial activity. Ethanol produced by the carbohydrates fermentation was identified in the five analyzed longaniza sausages and its area percentage varied between 2.03 and 29.26%. The samples presenting a lower area percentage of sulphur compounds presented a higher area percentage of ethanol, which resulted from the microbial fermentation.

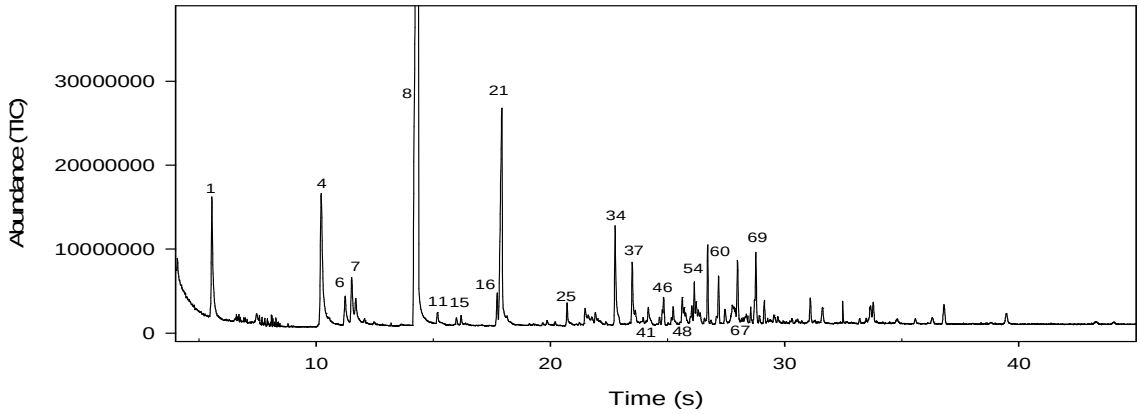

Figure 2 - Chromatogram obtained by SPME after exposition for 0.5 h at 30°C in the headspace of longaniza.

Hierro et al. (2004) reported that 2-methoxyphenol or guaicol showed antimicrobial activity. These were found in the samples 3, 4 and 5; however, it was not possible to relate their presence to the decrease of compounds generated by the fermentation.

The compounds derived from 2-cyclopenten-1-one were originated by the Maillard reaction through the pyrolysis of complex carbohydrates (cellulose) during the smoking process (Jerkovic et al. 2010). 3-hydroxi-2-butanone was identified in the five analyzed samples and its area percentage varied between 0.76 and 9.18%. This ketone was in dry cured loin (Muriel et al. 2004) and raw pork meat (Soncin et al. 2007).

Terpenes have two possible origins, fat deposit accumulation resulting from the animals feeding process or spices added during the elaboration process (Muriel et al., 2004). The presence of p-cymene has been previously reported in oregano (Baranauskiene et al. 2006).

Butyrolactone was identified in four out of five analyzed longaniza sausages samples. Ruiz et al. (2002) considered the presence of lactone in dry-cured Spanish ham as produced by the lipid oxidation, Maillard reactions and the heating process.

Hexanal was the only identified aldehyde in the samples. Nevertheless, it was present in two of the analyzed samples. Soncin et al. (2007) reported the presence of aldehydes in raw pork meat.

Hexanal and pentanal have been reported as lipid oxidation indicators in the meat (Brunton et al. 2000). Highest area percentage of volatile compounds resulting from the lipid oxidation reached 17.34%, compared to those values

obtained from the carbohydrates fermentation in the charqui samples that might reach an area percentage as high as 80.1%. These results showed that the predominant processes in the longaniza sausages were carbohydrates fermentation and it also showed that the lipid oxidation might occur in a low proportion.

It was concluded that the volatile compounds identified in the charqui samples mainly resulted from the lipid degradation reaction. These compounds could be used as volatile profile indicator. Four out of five charqui brands showed similar total area percentages for alcohols between 51-64% and aldehydes between 10-14%. However, there were significant statistical differences among the analyzed samples concerning the response area in particular of each volatile compound. In the longaniza sausages samples, the volatile compounds mainly came from the spices and raw materials used for their elaboration. The volatile compounds present in the samples headspace did not show similitude among the samples. The volatile compounds area percentages showed significant statistical differences.

CONCLUSIONS

Chilean traditional meat products, such as charqui and longaniza sausage showed different volatile compounds profile. The volatile compounds showed significant statistical differences among all the analyzed samples. However, charqui showed most volatile compounds resulting from the lipid oxidation. In the case of longaniza sausages, the volatile compounds resulted from the spices and carbohydrate fermentation. The differences between the two meat products were due to the raw materials and processing conditions. Charqui is a whole muscle dry product while longaniza is a fresh minced meat product.

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