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Food Chemistry 85 (2004) 649–657

Food Chemistry

www.elsevier.com/locate/foodchem

Analytical, Nutritional and Clinical Methods

Headspace volatile compounds from salted and occasionally smoked dried meats (cecinas) as affected by animal species

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Received 25 April 2003; received in revised form 28 July 2003; accepted 28 July 2003

Abstract

"Cecina" is a traditional intermediate moisture food prepared by salting, drying and, occasionally, smoking meat pieces. The stability and long shelf-life of these products are due to their low water activity (a_w), ranging from 0.90 to 0.60. The headspace volatile compounds from samples of dry meats from venison, beef, horse and goat cecina were analysed by gas chromatography–mass spectrometry (GC/MS) to characterise the volatile profile of these meat products. In general, about 110 volatile compounds were identified and quantified. Typical breakdown products derived from lipid oxidation, amino acid catabolism and carbohydrate fermentation were the main volatiles detected in all cecinas, together with the volatiles generated by the smoking process. However, horse cecina also presented important concentrations of esters and showed very few volatiles coming from the smoke.

Keywords: Headspace analysis; Volatile compounds; Cured meats; Cecina; Flavour

1. Introduction

Salting and drying were first used as common procedures for preserving meats. Salted and dried pork (dry-cured ham) chemical composition and volatile compounds have been described by many authors (Buscailhon, Monin, Cornet, & Bousset, 1994; López et al. 1992; Pérez, Sayas, Fernández, Gago, Pagán, & Aranda, 1999; Vestergaard, Schivazappa, & Virgili, 2000) but information about similar technology in meat of other animal species is scarce. Spanish "cecina" resembles South African "biltong", South American "charqui" and Italian "bresaola". Nowadays, these salted, dried meats, made from whole meat pieces of pork, beef, goat, venison and horse, represent a great variety of products, and their characteristic flavour is one of the key attributes for the consumer.

Its preparation consists basically of six stages. The first is the fine shaping to adapt the forms of the pieces, mainly back leg and sirloin. Then, the raw pieces are salted with coarse salt, forming piles alternating between pieces and salt; the salting stage duration has a minimum of 0.3 days and a maximum of 0.6 days per kg of meat at 2–5 °C and a relative humidity (RH) of 80–90%. After salting, the pieces are taken from the piles and washed off with warm water and transferred to a settling room where they stay for 30–45 days at 3–5 °C and RH 85–90%. Once the post-salting stage has finished, the pieces can be optionally smoked using firewood. Finally, the pieces undergo a ripening process in which they are transferred to drying areas at 12–20 °C and RH 65–80%. The bigger the meat piece size, the longer the ripening period (3–8 months).

Throughout this long ripening period the meat becomes progressively and partially dried to reach a stabilised microbial state ($a_w < 0.90$) and also acquires its characteristic properties of aroma and taste due mainly to the changes that take place in proteins and lipids (García, Díez, & Zumalacárregui, 1997, 1998; Zumalacárregui, & Díez, 2001).

Although these meats are mainly domestic products, they are now progressively entering several international markets. In order to obtain a quality competitive product, a normalised technology is necessary. To aid in this task, scientific assessment is needed to explain the

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doi:10.1016/j.foodchem.2003.07.001

peculiarities of these products. To date, several studies have been done in which microbiological, sensory and some physicochemical (pH, a_w, protein, fat, amino acids, fatty acids) characteristics of cecina (García et al., 1997, 1998; García, Zumalacárregui & Díez, 1995), bresaola (Bersani, d'Aubert, & Cantoni, 1991), charqui (Torres et al. 1994) and other dried meats (Paleari, Bersani, Moretti, & Beretta, 2002; Paleari, Moretti, Beretta, Mentasti, & Bersani, 2003) have been evaluated. However, there are no references about the volatile compounds extracted from these products.

The objective of this study was to identify and quantify the volatile compounds characteristic of cecinas prepared from venison, beef, horse and goat in an attempt to establish a volatile pattern according to species.

2. Materials and methods

2.1. Samples

Four different samples of cecina, elaborated by well-known meat companies, following the traditional method described briefly in the introduction section, were purchased. Each sample came from a different animal specie: deer, bovine, horse and goat. Horse cecina was prepared from sirloin (corresponding to muscle *longissimus dorsi*) while venison, bovine and goat were obtained from back leg (mainly composed of the muscles *semimembranosus*, *semitendinosus* and *biceps femoris*). They were vacuum packed and stored at 2–4 °C before being analysed (up to 1 month). Analyses were performed in three different samples of each animal species.

To avoid interferences from superficial mould growth or spices and condiments added, samples were taken after discarding the external layer (top 2 cm) of meat.

2.2. Chemical analysis

Dry matter (DM) was determined by drying the sample at 110 °C to constant weight.

2.3. Analysis of volatile compounds

Volatile compounds were analyzed by GC/MS, as described by Elmore, Mottram, Enser, and Wood (2000). Twenty-five grammes of each sample were introduced into a glass flask and equilibrated for 30 min at 30 °C. Volatiles were extracted at 30 °C by a nitrogen flow of 40 ml min^{-1} for 1 h and adsorbed on a steel trap (105 mm × 3 mm i.d.) containing 85 mg of Tenax TA (Scientific Glass Engineering Ltd., Milton Keynes, UK). A standard of 131 ng of 1,2-dichlorobenzene (Sigma) in 1 μl of methanol (Panreac) was added to the trap at the end of the collection and excess solvent and any water retained on the trap were removed by purging the trap with nitrogen at 40 ml min^{-1} for 5 min.

Analyses were performed on a Hewlett-Packard 5972 mass spectrometer fitted with a HP5890 Series II gas chromatograph and a G1034 Chemstation (Hewlett-Packard, Palo Alto, CA, USA). A CHIS injection port (Scientific Glass Engineering Ltd.) was used to thermally desorb the volatiles from the Tenax trap onto the front of a CP-Sil 8 CB low bleed/MS fused silica capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness, Chrompack, Middelburg, The Netherlands). During a desorption period of 5 min, volatile compounds were cryofocused by immersing 15 cm of column adjacent to the heater in a solid CO_2 bath while the oven was held at 40 °C. The bath was then removed and chromatography achieved by holding at 40 °C for 2 min followed by a programmed rise to 280 °C at 4 °C min^{-1} and held for 5 min. A series of *n*-alkanes (C_6–C_{22}) (Sigma) was analysed under the same conditions to obtain linear retention index (LRI) values for the aroma components.

The mass spectrometer was operated in electron impact mode with an electron energy of 70 eV and an emission current of 50 μA. Compounds were identified by first comparing their mass spectra with those contained in the HP Wiley 138 Mass Spectral Database and then comparing the LRI values with either those of authentic standards or with published values. Approximate quantities of the volatiles were estimated by comparing their peak areas with those of the 1,2-dichlorobenzene internal standard, obtained from the total ion chromatograms, using a response factor of 1. Analysis were performed in triplicate.

3. Results and discussion

The dry matter content of venison, beef, horse and goat cecina samples were 58, 56, 53 and 64%, respectively.

In total, 110 compounds were tentatively identified when analysing headspace of venison, beef, horse and goat cecina samples by GC/MS, although all the identified substances were not present in all of the analysed samples. Compounds from different chemical classes were identified including hydrocarbons, aldehydes, alcohols, ketones, furans, organic acids, esters, sulphur compounds, terpenes, pyridines and pyrazines. In the following sections, the volatile compounds were classified according to their most likely origin (Table 1).

3.1. Volatile compounds from lipid oxidation

Venison cecina samples showed the highest amount of lipid oxidation volatiles (6890 ng/100 g dry matter), followed by horse (5253 ng/100 g DM), goat (4655 ng/

Table 1
Volatile compounds (ng/100 g) identified in the headspace of cecinas

LRI[a]	Compound	Mean concentration (ng/100 g)				Method of identification[b]
		Venison	Beef	Horse	Goat	
	Lipid oxidation	**3996**	**2418**	**2784**	**2979**	
	Alcohols	394	562	1594	356	
560	1-Propanol	30	115	529	30	MS + LRI
653	1-Butanol	96	104	78	nd	MS + LRI
672	1-Penten-3-ol	94	60	656	227	ms + lri
705	2-Pentanol	nd	86	100	nd	MS + LRI
765	1-Pentanol	86	61	99	83	MS + LRI
862	1-Hexanol	46	65	109	16	MS + LRI
904	2-Heptanol	4	19	nd	nd	MS + LRI
980	1-Octen-3-ol	38	35	19	nd	MS + LRI
1075	1-Octanol	nd	17	4	nd	MS + LRI
	Aldehydes	1415	579	574	1255	
705	Pentanal	205	28	1	197	MS + LRI
802	Hexanal	961	144	428	806	MS + LRI
848	2-Hexenal (*E*)	nd	nd	1	nd	MS + LRI
902	Heptanal	142	113	40	136	MS + LRI
1005	Octanal	37	87	26	49	MS + LRI
1065	*E*,*E*-2,4-Heptadienal	nd	nd	3	nd	MS + LRI
1105	Nonanal	54	189	64	66	MS + LRI
1217	Decanal	16	18	11	1	MS + LRI
	Ketones	459	745	152	178	
683	2-Pentanone	197	571	148	99	MS + LRI
789	2-Hexanone	95	nd	nd	nd	MS + LRI
898	2-Heptanone	129	134	4	29	MS + LRI
980	2,3-Octanedione	nd	nd	nd	50	ms + lri
1099	2-Nonanone	38	40	nd	nd	MS + LRI
	Hydrocarbons	1703	472	396	1178	
600	Hexane	852	125	119	747	MS + LRI
700	Heptane	203	57	97	110	MS + LRI
792	1-Octene	nd	28	13	77	MS + LRI
800	Octane	183	147	124	114	MS + LRI
812	2-Octene	358	37	nd	11	MS + LRI
900	Nonane	62	26	19	60	MS + LRI
1000	Decane	31	40	22	27	MS + LRI
1092	1-Undecene	nd	12	nd	nd	MS + LRI
1100	Undecane	14	nd	2	32	MS + LRI
	Furans	25	60	68	12	
604	2-Methylfuran	nd	37	4	12	MS + LRI
701	2-Ethylfuran	12	12	64	nd	MS + LRI
994	2-Pentylfuran	13	11	nd	nd	MS + LRI
	Amino acid degradation	**1859**	**2835**	**4174**	**1380**	
551	2-Methylpropanal	72	102	97	113	MS + LRI
629	2-Methylpropanol	170	392	970	nd	ms + lri
654	3-Methylbutanal	818	1029	304	443	MS + LRI
662	2-Methylbutanal	186	419	96	141	MS + LRI
727	Dimethyl disulfide	53	42	nd	5	MS + LRI
730	4-Methyl-2-pentanone	nd	nd	nd	18	MS + LRI
740	3-Methylbutanol	412	682	2080	204	MS + LRI
744	2-Methylbutanol	72	105	194	nd	MS + LRI
752	3-Methyl-2-pentanone	56	47	346	101	ms + lri
857	3-Methylbutanoic acid	nd	nd	nd	223	ms + lri
868	2-Methylbutanoic acid	nd	nd	nd	47	ms + lri

(continued on next page)

Table 1 (*continued*)

LRI[a]	Compound	Mean concentration (ng/100 g)				Method of identification[b]
		Venison	Beef	Horse	Goat	
972	Benzaldehyde	15	10	21	85	MS + LRI
984	Dimethyl trisulfide	5	7	nd	nd	ms + lri
1065	Benzeneacetaldehyde	nd	nd	66	nd	MS + LRI
	Carbohydrate fermentation	**7825**	**1749**	**3294**	**4806**	
649	Acetic acid	160	15	nd	493	MS + LRI
587	2,3-Butanedione (*diacetyl*)	2809	251	92	1205	ms + lri
604	2-Butanone	446	383	310	nd	MS + LRI
666	1-Hydroxy-2-propanone	32	78	nd	48	ms + lri
711	3-Hydroxy-2-butanone (*acetoin*)	4205	539	173	2993	MS + LRI
503	Ethanol	80	391	2296	52	ms + lri
591	2-Butanol	93	92	423	15	MS + LRI
	Microbial esterification	**72**	**122**	**2790**	**104**	
531	Methyl acetate	10	8	13	3	ms
615	Ethyl acetate	45	85	1285	13	MS + LRI
685	Methyl-2-methyl-propanoate	nd	nd	8	nd	ms + lri
709	Ethyl propanoate	7	9	119	nd	MS + LRI
716	Propyl acetate	nd	nd	15	nd	MS + LRI
724	Methyl butanoate	4	6	3	nd	ms + lri
756	Ethyl-2-methyl-propanoate	nd	6	268	nd	ms + lri
	Methyl-3-methyl-butanoate	nd	nd	17	nd	ms
782	2-Methyl propanoate	nd	nd	nd	88	ms + lri
805	Ethyl butanoate	nd	nd	115	nd	MS + LRI
846	Ethyl-2-methyl butanoate	nd	nd	211	nd	MS + LRI
849	3-Methylethyl butanoate	6	8	669	nd	MS + LRI
877	3-Methylbutyl acetate	nd	nd	17	nd	ms + lri
879	2-Methylbutyl acetate	nd	nd	2	nd	ms + lri
901	Ethyl pentanoate	nd	nd	6	nd	MS + LRI
	3-Methylpropyl butanoate	nd	nd	5	nd	ms
997	Ethyl hexanoate	nd	nd	27	nd	MS + LRI
	3-Methylbutyl-3-methyl butanoate	nd	nd	6	nd	ms
1196	Ethyl octanoate	nd	nd	4	nd	MS + LRI
	Smoke	**1995**	**3565**	**271**	**2526**	
	Phenolic compounds	108	662	26	427	
992	Phenol	30	128	8	151	MS + LRI
1071	2-Methyl-phenol (*o-cresol*)	9	55	3	53	ms
1086	4-Methyl-phenol (*p-cresol*)	nd	44	8	49	ms + lri
1091	2-Methoxyphenol (*guaiacol*)	60	370	7	154	ms
	4-Methyl-2-methoxyphenol (*4-methylguaiacol*)	9	65	nd	20	ms
	Cyclopentanones/enones	121	1199	8	273	
795	Cyclopentanone	nd	571	nd	75	ms
847	2-Methylcyclopentanone	62	331	nd	19	MS + LRI
858	3-Methylcyclopentanone	17	35	8	10	ms
915	2-Methyl-2-cyclopenten-1-one	14	76	nd	39	ms
973	3-Methyl 2-cyclopenten-1-one	28	102	nd	86	ms
	2,3-Dimethyl-2-cyclopenten-1-one	nd	73	nd	44	ms
1076	a Trimethyl-2-cyclopenten-1-one	nd	11	nd	nd	se
	Aromatic hydrocarbons	1568	503	231	1546	
663	Benzene	28	56	49	62	MS + LRI
769	Methylbenzene (*toluene*)	1387	192	118	1260	MS + LRI
864	Ethylbenzene	36	23	12	59	MS + LRI
865	a Dimethylbenzene	75	43	28	134	ms
893	Vinylbenzene (*styrene*)	nd	109	1	nd	MS + LRI
971	1-Ethyl-2-methylbenzene	15	35	11	nd	ms
1012	1,2,3-Trimethylbenzene	27	45	12	31	ms

Table 1 (*continued*)

LRI[a]	Compound	Mean concentration (ng/100 g)				Method of identification[b]
		Venison	Beef	Horse	Goat	
	Furans	133	871	2	158	
839	2-Furancarboxaldehyde (*furfural*)	14	58	nd	12	ms + lri
856	2-Furanmethanol (*furfuryl alcohol*)	119	813	2	146	MS + LRI
	Pyridines	52	275	nd	28	
751	Pyridine	46	182	nd	16	MS + LRI
818	2-Methylpyridine	6	51	nd	8	ms
869	3-Methylpyridine	nd	42	nd	4	ms
	Pyrazines	13	55	4	94	
833	Methylpyrazine	5	23	1	16	MS + LRI
912	2,6-Dimethylpyrazine	5	12	3	36	MS + LRI
924	Ethylpyrazine	nd	12	nd	nd	MS + LRI
1014	Trimethylpyrazine	3	8	nd	42	MS + LRI
	Spices	**1683**	**234**	**191**	**206**	
934	α-Pinene	nd	24	8	51	ms + lri
946	Camphene	nd	13	3	20	ms + lri
956	2-Ethyl-hexanal	31	nd	nd	nd	ms
1031	Limonene	14	197	33	135	MS + LRI
1037	2-Ethyl-hexanol	1638	nd	147	nd	ms
	Unknown origin	**1284**	**1865**	**574**	**307**	
	2-Propanone	1072	813	300	186	MS + LRI
524	2-Propanol	212	1052	274	22	MS + LRI
818	Butanoic acid	nd	nd	nd	99	MS + LRI
	Total volatiles	**18 714**	**12 788**	**14 078**	**12 308**	

[a] Linear retention index on a CP-Sil 8 CB low bleed/MS column.

[b] MS + LRI, mass spectrum and LRI agree with those of authentic compounds; ms + lri, mass spectrum and LRI in agreement with the literature; ms, mass spectrum agrees with spectrum in the HP Wiley 138 Mass Spectral Database; se, tentative identification by mass spectrum.

nd: not detected.

100 g DM) and beef (4318 ng/100 g DM). These results agreed with the quantity of polyunsaturated fatty acids (PUFA), which are autooxidation substrates, recorded in the intramuscular fat of cured meats from these species (Paleari et al., 2003). When determining the fatty acid composition, these authors found that PUFA were more elevated in the cured meats of horse and deer, followed by goat, and extremely reduced in bovine samples. The results were also in agreement with the piece size used for drying. The smallest were those from venison and goat with a final weight ranging from 1.5 to 4 kg. A similar conclusion may be drawn with cecina from horse since the sirloin separated from the carcass was used for manufacturing the dry meat. The greatest size pieces were those coming from beef since the individual back legs were used for drying. Accordingly, the accessibility of the atmospheric oxygen to the piece was lower and, consequently, the final product showed a lower level of autooxidation substances than those detected in the other species.

Straight-chain aliphatic aldehydes are typical products of lipid oxidation with very low odour thresholds (Shahidi, Rubin, & D'Souza, 1986). Saturated aliphatic aldehydes from C_5 up to C_{10} were detected in all samples. Hexanal was the principal component of these compounds in horse, venison and goat cecina, reaching, in the latter, 27% of all volatiles generated via lipid oxidation. Hexanal has also been detected at high levels in both dry fermented sausages (Bruna et al., 2001; Edwards, Ordóñez, Dainty, Hierro, & Hoz, 1999) and dry-cured hams (García et al., 1991; Ruiz, Ventanas, Cava, Andrés & García, 1999). Its aroma has been described as strong, rancid, unpleasant (MacLeod & Coppock, 1976), hot, nauseating (Persson & von Sydow, 1973), green leaves, vegetables (Stahnke, 1994), from which it can be concluded that hexanal must have an effect on the cecina aroma, although it is modulated by other aromatic compounds accumulated at the same time.

Although hydrocarbons reached high concentrations in all samples, being the main volatiles formed via lipid oxidation in venison cecina, they probably have no significant impact on flavour as they have relatively high odour threshold values (Drumm & Spanier, 1991).

Other molecules derived from lipid oxidation were the methylketones, although they are less important in the flavour of meat products as they have odour threshold values higher than those of their isomeric aldehydes (Seik, Albin, Sather, & Lindsay, 1971). The methylketones may originate from fatty acids through chemical (auto-oxidation) or enzymatic (β-oxidation) reactions during mould metabolism. This last via is possible, since an important superficial fungal growth has been reported in cecinas during the drying phase in a cellar (Dragoni, Cantoni, & Papa, 1990; Zumalacárregui & Díez, 2001), and although the cecina superficial layer was discarded, some of the compounds may have diffused to the cecina core. This possibility seems to be confirmed by the fact that the formation of methylketones by moulds involves a decarboxylation in the metabolic pathway (Dartey & Kinsella, 1973). Therefore, the formed methylketone has an odd carbon atom number. Furthermore, the methylketones may be reduced to secondary alcohols. This is the case with two methylketones detected and the corresponding alcohols, i.e. 2-heptanone and 2-heptanol, and 2-pentanone and 2-pentanol, are produced, respectively, from octanoic (caprylic) and hexanoic (caproic) acids. Moreover, when the level of methylketone was low, (e.g. 2-heptanone in horse and goat or 2-pentanone in goat), the secondary alcohol was also low or was not detected.

3.2. Volatile compounds from amino acid degradation

The main volatiles in this group were branched aldehydes and their corresponding alcohols, which can be derived from amino acids via Strecker degradation (Barbieri, Bolzoni, Parolari, & Virgili, 1992; García et al., 1991; Ventanas et al., 1992) or by microorganisms (Degorce-Dumas, More, Goursaud, & Leveau, 1984; Hinrichsen & Pedersen, 1995). The former pathway has been proposed in dry-cured ham (Ventanas et al., 1992); this hypothesis is based on the favourable values of several parameters (water activity, pH, temperature and the time of processing) which should allow such reactions to develop. On the other hand, a microbial origin is also possible, since some microorganisms such as *Streptococcus lactis* var. *maltigenes*, *Staphylococcus xylosus*, *Staphylococcus carnosus* and halotolerant *Vibrio* spp., are able to form branched aldehydes and their corresponding alcohols from amino acids (Hinrichsen & Andersen, 1994; MacLeod & Morgan, 1955; Stahnke, 1999). *S. xylosus* is one of the dominant species isolated in dry-cured hams (Cornejo & Carrascosa, 1991), bresaola (Bersani et al., 1991) and beef cecina (García et al., 1995). Therefore, in cecinas both formation routes are feasible. A high content of free amino acids is a characteristic feature of cecina, especially of the precursors of these branched aldehydes (valine, isoleucine and leucine) which are among the most abundant in final products prepared with meats from different animal species (García et al., 1998; Paleari et al., 2003). This fact supports the amino acid origin of these compounds. The higher content of amino acid-derived volatiles registered in beef cecina might be due to the longer drying process of these samples (up to 6 months), as the pieces are heavier than those of venison and goat. The horse cecina also showed a great abundance of these compounds. However, it can not be explained as in beef because the processed meat piece, the sirloin, was smaller. In this case, the amino acid breakdown may be attributed to a greater number of microorganisms during ripening. This justification is consistent with the high levels of esters detected; it has been well demostrated that they are formed by microbial activity (Hosono, Elliot, & McGugan, 1974; Stahnke, 1995).

2-Methylpropanal, and 2- and 3-methylbutanal have been associated with a ripened aroma in cured meat products (Careri, et al., 1993; Ruiz et al., 1999; Søndergaard, & Stahnke, 2002). They can be transformed, as well, into their corresponding alcohols, acids and even esters, as all of these compounds are of great importance in the final flavour of cecinas.

3.3. Volatile compounds from carbohydrate fermentation

Venison cecina showed the highest levels of volatile compounds from fermentation of carbohydrates, followed by goat, horse and beef. 3-Hydroxy-2-butanone (acetoin) and 2,3-butanedione (diacetyl) were the most abundant volatiles of this group in venison cecina. These compounds impart butter and cheese odour. Diacetyl also has a characteristic sweet odour and a low sensory threshold and, according to Stahnke (1995), is of great importance to the final aroma. A higher concentration of fermentation compounds in venison and goat cecina could indicate a higher metabolic activity of the microbiota of these samples. As has been stated previously, *S. xylosus* is the most representative specie in cecinas, and it has been shown that this organism produces diacetyl, 2-butanone and acetoin (Søndergaard & Stahnke, 2002).

3.4. Volatile compounds from microbial esterification

Esters were the group of compounds which showed the highest differences among the various cecinas. In this way, 2790 ng/100 g have been found in horse cecina while, in venison, beef and goat, these compounds were hardly detected (72, 122 and 104 ng/100 g, respectively). The most abundant esters were the ethyl-esters, which are generated from the esterification of ethanol and organic acids by microbial esterases (Stahnke, 1995). Ethanol is mainly derived from carbohydrate fermentation, i.e. lactic acid bacteria, which may divert the

homolactic pathway at the level of pyruvate, yielding ethanol by the system pyruvate formate lyase (Kandler, 1983). On the other hand, free fatty acids are generated as a result of the action of lipases. It is remarkable that ethanol was found in high levels in horse cecina, with a value 44-, 29- and 6-fold higher than those registered for goat, venison and beef samples, respectively. The higher ethanol content in horse cecina could be attributed to a higher glycogen concentration in horse meat. Lawrie (1998) showed values of glycogen in *longissimus dorsi* of 2249 mg/100 g in horse and 957 mg/100 g in steer. Also, the higher level of ethanol detected in horse cecina could be related to the higher load of lactic acid bacteria found in horse meat. In this sense, Paleari et al. (2002) studied the microflora present in raw and dry meat of deer, bovine, goat and horse, finding that lactic acid bacteria were the dominant flora in both raw and dry horse meat, reaching levels of 10^7 and 10^9 cfu/g, respectively. The levels of these microorganisms detected in raw bovine, deer and goat meat were much lower (3, 2 and 2 logarithmic units less, respectively) and 2 logarithmic units less for dry bovine meat and around 1 logarithmic unit for the dry meat of the other species. Both facts, higher glycogen content and higher lactic acid bacteria counts could also explain the higher ethyl-ester concentrations formed in horse cecina samples. It is well documented that many strains of lactic acid bacteria used as starter cultures are able to produce esters (Hosono et al., 1974; Liu, Holland, & Crow, 1998).

Esters have been reported as important volatiles in fermented sausages (Edwards et al., 1999; Stahnke, 1994) and they are also present, although in lower levels, in dry-cured ham (Buscailhon, Berdagué, & Monin, 1993; Ruiz et al., 1999; Ruiz, Ventanas, & Cava 2001) due to the low microbial count found. They have low odour threshold values and impart fruity notes (Stahnke, 1994), and they have been associated, together with branched aldehydes, to ripened flavour in cured meat products (Barbieri et al., 1992; Careri et al., 1993; Montel, Reitz, Talon, Berdagué, & Rousset-Akrim, 1996).

3.5. Volatile compounds from smoke

As was expected from a smoked meat product, typical wood smoke compounds were quantified among the headspace volatiles isolated from cecina. After the post-salting stage, the pieces can be smoked and the smoking process is more or less intense depending on the manufacturer. The removal of the external 2 cm layer does not prevent the detection of smoke compounds since it has been reported by Stofila (1999) that there is a diffusion of these compounds into the core of the piece with a maximum concentration at surface layers which sharply decreases towards the sample axis. Beef cecina showed the highest levels of these compounds, which indicates that this sample underwent an intense smoking process. The volatiles identified and quantified in all samples were cyclopentanones, cyclopentenones, aromatic hydrocarbons, furans, pyridines, pyrazines and phenolic compounds, all of which are characteristic compounds of wood smoke (Maga, 1987; Tóth & Potthast, 1984). The low sensory threshold values of phenolic compounds make them important contributors to the flavour of cecina. Guaiacol, *o*-cresol and *p*-cresol are powerful aromatic compounds with odour threshold values between 0.1 and 1 ng/l (Rychlik, Schieberle, & Grosch, 1998).

3.6. Volatile compounds from spices

Occasionally, the pieces are superficially covered with a mixture of salt and spices. Only venison cecina showed important levels of volatile compounds resulting from the added spices. The dominant compound in this sample was 2-ethyl-hexanol which could come from pepper (Sunesen, Dorigoni, Zanardi, & Stahnke, 2001).

4. Conclusions

Within the headspace of cecina is a complex mixture of volatile compounds. Lipid oxidation, amino acid degradation and carbohydrate fermentation are the main pathways of volatile generation in cecinas; smoke-derived compounds are also important in those products which have undergone an intense smoking process. Only horse cecina showed relevant ester levels.

Acknowledgements

The authors wish to thank Dr. D.S. Mottram for the provision of GC/MS equipment in the analysis of volatiles. This work has been supported by the Universidad Complutense de Madrid with the PR48/01-9879 project.

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