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Effect of packaging material on volatile organic compounds (VOCs) of sliced and MAP packaged typical Italian and Spanish dry-cured hams

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Abstract. The volatile organic compounds (VOCs) of Parma and Teruel dry-cured hams were studied, by comparing fresh and MAP (modified atmosphere packaging) sliced products. Two polymeric food-grade packaging materials were used for ready-to-eat packages of pre-sliced dry-cured hams: PET (polyethylene terephthalate) with barrier film PET/EVOH/PE (polyethylene terephthalate / ethylene-vinyl alcohol / polyethylene copolymer) and PLA (polylactic acid) with PLA barrier film. Several differences in VOCs were attributed to dry-cured ham nature, with ethyl esters being a main feature of Parma ham, while compounds generated by amino acids catabolism prevailed in Teruel ham. Packaging in PLA increased VOCs originated from lipid oxidation, more abundant in Parma hams, and from amino acid catabolism, while packaging in PET increased the signals due to branched-chain alkanes (BCAs). VOCs originated from carbohydrate fermentation were negligibly affected by packaging material, while a dependence from the nature of dry-cured ham was observed.

Keywords. Dry-cured ham – Packaging material – Volatile organic compounds – Polylactic acid.

Effet du matériel de conditionnement sur les composés organiques volatils (COV) des jambons italiens et espagnols en tranches et conditionnés en atmosphère modifiée

Résumé. *Les propriétés du jambon de Parme et du jambon de Teruel en termes de composés organiques volatils (COV) ont été comparées, par comparaison entre les produits frais en tranches et les produits emballés en atmosphère modifiée. Pour le conditionnement du jambon prétranché on a utilisé deux matériaux d'emballage de qualité alimentaire, consistant en deux polymères différents: PET standard (polyéthylène téréphtalate) avec barrière PET / EVOH / PE (polyéthylène téréphtalate / éthylène-alcool vinylique / copolymère de polyéthylène) et PLA (acide polylactique) avec des films barrière en PLA. Plusieurs des différences de COV observées sont attribuées à la nature du jambon, notamment les esters éthyliques qui caractérisent le jambon de Parme, et au contraire, les composés produits par le catabolisme des acides aminés ont plus d'impact dans le Jambon de Teruel. L'emballage en PLA a montré une augmentation des COV originaires de l'oxydation des lipides et du catabolisme des acides aminés, alors que l'emballage en PET a causé une augmentation de l'intensité d'alcanes à chaîne ramifiée (BCAs). Les COV provenant de la fermentation des glucides ont été négligeablement affectés par le matériel d'emballage, tandis que leur dépendance par rapport à la nature du jambon a été démontrée.*

Mots-clés. *Jambon – Matériaux d'emballage – Composés organiques volatils – Acide polylactique.*

I – Introduction

Protective atmosphere packaged (MAP) pre-sliced dry-cured hams gained in recent years a positive commercial trend (+7.8% in 2009, source: Consortium of Parma ham, 2010). Recent studies (Parolari *et al*., 2009) reported the occasional onset of changes in MAP packaged dry-cured hams, impairing colour, odour and taste. The standard packaging material used for dry-cured ham is the food-grade polyethylene terephthalate (PET). Meanwhile, new materials have been investigated, taking into account environmental sustainability too. Among them, the biopolymer polylactic acid (PLA) has grabbed attention because it is synthesized from processed corn and it biodegrades after use. PLA is regarded like a "natural" package with good flavor retention; a limiting factor for PLA is its relatively poor barrier to water vapor and O_2 (Rhim *et al*., 2009). In this study, the VOCs were investigated, to focus differences due to ham nature and packaging.

II – Materials and methods

Four Parma (P) and 4 Teruel (T) dry-cured hams, aged 17-20 months, were sliced and packaged in PLA and PET with N_2:CO_2 = 70:30 MAP. Each package was filled with 85-90 g of 15 mm-thick slices. VOCs analysis was carried out on fresh and packaged slices (starting 2 weeks after packaging): 3 g, finely cut with a knife, were subjected to HS-SPME-GC-MS with a CAR/PDMS/DVB fiber (Supelco) for 120 min at 40°C, according to the method of Pinna *et al*. (2009). Data were checked for normal distribution and analyzed by the General Linear Model (GLM) procedure of SPSS ver. 11.5. The calculated model included ham nature and packaging as main effects. The Least Square Means (LSM) were estimated and the Bonferroni t-test was performed to statistically separate them. Principal Component Analysis (PCA) was run and scores of ham samples were graphically plotted onto the PC1-PC2 plane.

III – Results and discussion

Aroma compounds are reported in Table 1 and grouped according to origin mechanism.

Table 1. Effect of ham nature and packaging type on VOCs (expressed in AU × 10^{-4})

Volatile compounds†	Ham nature (N)		Packaging (P)			Significance			Loadings††	
	Parma	Teruel	None	PET	PLA	N	P	O x P	PC1	PC2
Lipid Oxidation										
1-Pentanol	95.8^{a}	46.9^{b}	54.6^{b}	54.8^{b}	105^{a}	***	***	ns	0.63	0.04
Pentanal	72.4^{a}	30.6^{b}	51.2	49.2	54.3	***	ns	ns	0.71	0.04
Hexane	9.70	5.46	7.94	7.76	7.14	*	ns	ns		
1-Hexanol	152	88.6	69.5	119	172	*	*	ns	0.52	0.29
Hexanal	440^{a}	143^{b}	225	248	401	***	*	ns	0.79	0.16
Heptane	27.6^{a}	15.1^{b}	17.1	17.8	29.2	**	ns	ns	0.66	0.05
Heptanal	152^{a}	63.8^{b}	89.7	98.7	136	***	ns	ns	0.79	0.17
2-Heptenal	7.23^{a}	2.82^{b}	4.69	2.99	7.39	**	ns	ns		
3-Heptanone	173	136	97.6^{b}	116^{b}	250^{a}	ns	***	ns		
Heptanoic Acid	268^{a}	103^{b}	139^{b}	159^{ab}	254^{a}	***	**	ns	0.86	0.19
Octane	184.3^{a}	97.1^{b}	100.4	119.6	201.9	**	*	ns	0.66	0.14
Octanal	54.3^{a}	26.5^{b}	41.1	39.2	41.0	***	ns	ns	0.70	0.11
1-Octen-3-ol	54.1^{a}	29.9^{b}	17.8^{b}	30.3^{b}	78.0^{a}	**	***	ns	0.59	0.11
Nonane	5.19^{a}	3.17^{a}	2.88^{b}	3.48^{b}	6.20^{a}	**	***	ns		
2-Nonanone	12.9	9.51	9.53	8.32	15.8	*	ns	ns	0.50	-0.06
2-Decenal	12.2^{a}	4.1^{a}	4.49^{b}	8.53^{ab}	11.4^{a}	***	***	*	-0.38	0.76
Undecane	18.5	24.5	12.1^{b}	33.9^{a}	18.5^{ab}	ns	***	ns	0.63	0.04
Carbohydrate fermentation										
Ethanol	679^{a}	317^{b}	410	485	762	***	ns	ns	0.62	0.28
Acetic Acid	78.2	63.8	63.6	57.8	91.6	ns	*	ns	0.62	-0.08
2-Butanone	40.3^{b}	77.0^{a}	66.0	60.1	49.9	***	ns	ns	-0.64	-0.29
2,3-butanedione	3.27^{b}	4.67^{a}	3.63	3.71	4.56	**	ns	ns		
3-hydroxy-2-butanone	99.1^{b}	165.9^{a}	152.4	138.1	107.0	**	ns	ns	-0.57	-0.03
Butanoic Acid	163^{a}	104^{b}	132	117	151	***	ns	ns	0.71	-0.07

Table 1. (*cont.*) Effect of ham nature and packaging type on VOCs (expressed in AU × 10^{-4})

Volatile compounds†	Ham nature (N)		Packaging (P)			Significance			Loadings††	
	Parma	Teruel	None	PET	PLA	N	P	O x P	PC1	PC2
Amino acid catabolism										
2-Methyl-propanal	13.1^{b}	24.7^{a}	16.5^{b}	18.1^{ab}	22.2^{a}	***	**	ns	-0.61	-0.19
3-Methyl-thio-propanal	10.5^{b}	17.4^{a}	9.54^{b}	10.5^{b}	21.8^{a}	**	***	**		
2-Metihyl-1-butanol	32.8	35.3	21.9^{b}	29.5^{ab}	50.7^{a}	ns	**	ns		
2-Methyl-butanal	127^{b}	254^{a}	161	209	201	***	ns	ns	-0.67	-0.05
3-Metihy-butanal	189^{b}	267^{a}	205	223	257	***	ns	ns		
Dimethyl-sulfide	2.32^{b}	3.75^{a}	4.58^{a}	3.38^{a}	1.15^{b}	**	***	ns	-0.53	-0.24
Dimethyl-disulfide	35.9	56.3	28.0	56.5	53.8	*	*	ns		
Toluene	89.5^{b}	156^{b}	112	112	144	**	ns	ns		
Phenyl-Ethyl-alcohol	11.2^{a}	3.60^{b}	2.40^{b}	6.13^{b}	13.7^{a}	***	***	ns	0.64	0.37
Esterase activity										
Ethyl acetate	4.84^{a}	2.56^{b}	3.26	3.59	4.25	***	ns	ns	0.64	0.25
Ethyl pentanoate	3.99^{a}	0.96^{b}	1.71	2.23	3.50	***	*	*	0.81	0.34
Ethyl hexanoate	53.6^{a}	12.4^{b}	22.3	29.6	47.2	***	ns	ns	0.81	0.33
Ethyl heptanoate	1.39^{a}	0.28^{b}	0.42^{b}	0.72^{ab}	1.36^{a}	***	***	*	0.81	0.35
Ethyl octanoate	9.23^{a}	4.31^{b}	6.29	5.64	8.39	***	ns	ns	0.70	0.18
Ethyl decanoate	6.70^{a}	3.26^{b}	5.27	4.04	5.58	**	ns	ns	0.58	0.12
Packaging contaminants										
2-ethyl-hexene	12.1^{a}	6.47^{b}	11.2^{a}	7.08^{b}	9.53^{a}	***	**	ns	0.51	-0.26
BCA 1	40.4	72.4	39.1^{b}	101^{a}	28.5^{b}	*	***	ns	-0.64	0.54
BCA 2	5.38	8.18	5.11^{b}	11.4^{a}	3.80^{b}	*	***	ns	-0.63	0.67
BCA 3	3.40	4.56	3.46^{ab}	5.93^{a}	2.54^{b}	ns	***	ns	-0.59	0.62
BCA 4	5.7^{b}	12.5^{a}	3.01^{b}	20.8^{a}	3.57^{b}	**	***	ns	-0.60	0.67
BCA 5	47.8^{a}	35.2^{b}	28.4^{b}	67.5^{a}	28.4^{b}	**	***	**	0.07	0.61
BCA 6	40.6^{a}	13.2^{b}	14.3^{b}	30.1^{a}	36.5^{a}	***	***	*	0.79	0.49
BCA 7	15.6	31.1	4.71^{b}	61.7^{a}	3.73^{b}	ns	***	ns	-0.55	0.68
BCA 8	2.91	2.56	1.93^{b}	0.23	0.99^{b}	ns	***	ns	-0.12	0.50
BCA 9	3.20	5.62	1.27^{b}	9.52^{a}	2.43^{b}	ns	***	ns	-0.51	0.73
BCA 10	16.0^{a}	11.7^{b}	14.8	12.3	14.4	**	ns	ns	0.50	0.01
Unknow origin										
Acetal	2.57	2.85	2.72^{ab}	1.44^{b}	3.99^{a}	ns	**	ns		
Ethylbenzene	113	141	69.3^{b}	180^{a}	132^{a}	ns	***	ns		
p-xylene	111^{b}	155^{a}	83.9^{b}	178^{a}	137^{ab}	ns	**	ns	-0.50	0.39
m-xylene	39.0^{b}	67.8^{a}	35.4^{b}	70.9^{a}	53.9^{ab}	***	*	ns	-0.64	0.30
Cyclohexane	3.50	2.97	4.87^{a}	1.70^{b}	3.15^{ab}	ns	***	ns	0.15	-0.66
Butyl-cyclohexane	13.1	12.9	15.4^{a}	8.19^{b}	15.4^{a}	ns	***	ns	0.28	-0.61
3-Methyl-penthyl-cyclohexane	5.96	6.14	8.60^{a}	3.53^{b}	6.04^{ab}	ns	**	ns	0.19	-0.62

†Only VOCs with a significant effect were reported. Significant effect : * P<0.10; ** P<0.05 ; *** P<0.01. Estimated means within a row with different lower case letters are different (P<0.05).
††Only variable loadings ≥ ± 0.5 on PC1 or PC2 are reported.

The compounds originating from the oxidative decomposition of lipids were most abundant in the Parma hams; oxidation compounds proved to be increased by PLA packaging. Dry-cured ham nature accounted for difference in compounds from carbohydrate fermentation. VOCs produced from amino acid catabolism were detected mostly in Teruel hams and were increased by PLA packaging. According to these results, the "breathable" PLA plays an effective role in enhancing both oxidation and maturation mechanisms. Ethyl esters were a feature of P hams, formed from free fatty acids with the high amount of ethanol found in these hams. Branched chain alkanes (BCAs) could not be identified with the available libraries and were named with subsequent numbers. These compounds increased significantly in PET packaging, as a possible consequence of migration from packaging material in direct contact with the ham slices, favoured by fat content (range 10-18% on wet slice) and high surface/volume ratio. Also ethylbenzene, m- and p-xylene increased in PET packaging. Principal Components Analysis (PCA) was carried out including VOCs listed in Table 1, and the scores of fresh (F) and packaged samples were plotted onto the PC1-PC2 plane (Fig. 1). P-PET and T-PET packaged hams differed from the fresh ones (P-F and T-F) along PC2, mainly discriminated by the BCAs content (Table 1). PLA packaged P (P-PLA) hams differed remarkably from the fresh P hams along PC1 and PC2 (increase of oxidation compounds, see Table 1). F and PLA packaged T samples are grouped closely, showing the stability of T hams in PLA.

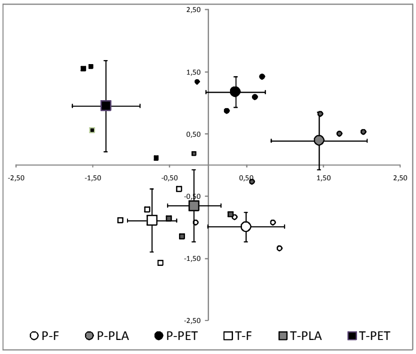

Fig. 1. Scoreplot of fresh and packaged sliced dry-cured hams. Large symbols represent the mean scores of each ham group, small symbols represent single samples, thin bars represent standard deviations of PC1-PC2 scores within groups.

IV – Conclusions

VOCs of Parma and Teruel dry-cured hams showed remarkable differences as a consequence of different processing way and formulation. Packaging in PLA material stressed differences between ham types, mainly due to the sharp increase of compounds generated by lipid oxidation in Parma ham. The effect of PET packaging was the rise of BCAs in both ham types, as a possible consequence of migration from packaging material in direct contact with the product. The improvement of safety and quality of ready-to-eat packaged dry-cured meat products will require further research on packaging materials.

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