EFFECT OF NATURAL AND SYNTHETIC ANTIOXIDANTS ON PHYSICO-CHEMICAL CHARACTERISTICS OF LIVER PÂTÉ

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Abstract – The effect of two natural antioxidant extracts (tea and seaweed) and one synthetic (BHT) on lipid oxidation (TBARS and peroxide index), pH and colour stability in liver pâtés from Celta pigs was evaluated. Pâtés were analyzed at 0, 4 and 24 weeks of refrigerated stored (4 ºC). No significant evolution (P>0.05) in each batch for pH, colour and TBARS were detected during refrigerated storage, except for peroxide index which gradually decreased during storage of pâtés. In each sampling point, the pâtés with different antioxidants showed significant differences in a*, b*, TBARS and peroxides. The lowest values of TBARS and peroxide index were showed by tea and BHT samples, respectively.

Key Words – lipid oxidation, seaweed extract, tea extract.

I. INTRODUCTION

Porcine liver pâté is a traditional cooked meat product consumed in many countries. It consists of minced liver, fat and meat mixed with water and different additives, which is packed in glass containers followed by a thermal treatment. Due to chemical composition of pâtés (high amounts of fat and non-haem iron) and its manufacturing process, this product is highly susceptible to lipid oxidation [1-2]. An alternative against oxidation process is the inclusion of antioxidants. Synthetic antioxidants, such as tert-butyl-4-hydroxytoluene (BHT), have proved effective as inhibitor of lipid oxidation and because of this are largely used in the food industry. However, the use of this synthetic compounds have been linked to health risks (carcinogenic potential) and currently research tends for their replacement by natural antioxidants [3]. Alternative substances, as tea and seaweed extracts, have showed antioxidant activity [4-6] and consequently could be introduced in meat products to control oxidative deterioration.

The aim of this work was to evaluate the effect of the addition of natural antioxidants (tea and seaweed extracts) on the lipid oxidative, pH and colour stability of refrigerated stored pâtés and compare this effect with that showed by a synthetic antioxidant (BHT).

II. MATERIALS AND METHODS

A. Experimental design and sampling

Four batches of pâté were manufactured in our pilot plant: A (control), B (BHT, 200 mg/kg), C (tea extract, 200 mg/kg) and D (seaweed extract, 200 mg/kg). An identical formula was used for all batches, except for the addition of the different antioxidants. The ingredients (%) were as follows: subcutaneous fat (40%), lean meat (15 %), liver (18%), cold water (23%), sodium chloride (2%) and sodium caseinate (2%). Fat, meat and liver were from Celta pig breed. Firstly, fat and liver were chopped in small cubes and scalded at 65 ºC for 10 min. The cooked fat and liver, after being allowed to cool at room temperature, were mixed with the remaining ingredients in a Talsa bowl chopper (Talsabell, S.A., Valencia, Spain). After that, total mass was divided in four batches of 3 kg each one. Antioxidants (BHT, tea extract and seaweed extract) were added in the corresponding batch (B, C and D, respectively) and the mass was mixed with a beater. Finally, the mixture was packed in glass containers and cooked by immersion in a hot water bath at 80 ºC for 30 min. After the recipients were allowed to cool at room temperature, they were stored in dark at 4 ºC for 24 weeks.

Two units of pâté from each batch were taken at 0, 4 and 24 weeks to determine the following parameters: pH, colour parameters, thiobarbituric acid reactive substances (TBARS) and peroxide index.

B. Analytical methods

The pH of samples was measured directly using a pH-meter (HI 99163, Hanna Instruments, Eibar, Spain) equipped with a glass probe for penetration. Instrumental colour in the CIELAB space (lightness: L*, redness: a* and yellowness: b*) [7] was automatically measured on the surface of pâté by a CM-600d portable colorimeter (Konica Minolta Sensing, Osaka, Japan). Peroxide index and TBARS were measured to assess primary and secondary lipid oxidation, respectively. Peroxide index (mEq O_2/kg fat) was determined following the AOAC Official Method 965.33 [8] after extraction of the fat according to Folch *et al*. (1957) [9]. TBARS index was measured according to the method of Vyncke (1975) [10]; results were expressed as milligrams of malondialdehyde (MDA) per kilogram of meat.

C. Statistical analysis

Physico-chemical results were statistically analysed using the SPSS package (SPSS 18.0, Chicago, USA). One-way analysis of variance (ANOVA) and a posterior Duncan´s test with a 0.05 level of significance were performed.

III. RESULTS AND DISCUSSION

Table 1 shows the evolution of pH, colour parameters, TBARS and peroxide index of each batch of pâté during refrigerated storage. At initial day, no significant differences ($P>0.05$) were detected for pH values among batches. However, at weeks 4 and 24, samples with antioxidants showed pH values significantly lower ($P<0.01$) than that for control batch. Within each batch, there were no significant differences ($P>0.05$) during refrigerated storage.

Colour parameters (L*, a*, b*) of liver pâtés of each batch did not significantly change ($P>0.05$) during storage. These results are not agree with those obtained by other authors [11-12] studying the colour deterioration during refrigerated storage of pâtés; these authors reported an increase of L* and a decrease of a* and b* during refrigeration. Among batches, the addition of antioxidants did not have a significant effect on L*, a* and b* values in each sampling point, except for the tea extract. In fact, samples with tea extract showed lower values of redness and yellowness than the other samples (2.3-2.5 and 15.6-16.0 *vs.* 4.1-4.7 and 18.4-19.6 for a* and b*, respectively).

Lipid oxidation is a complex process in which unsaturated fatty acids react with molecular oxygen via a free radical chain mechanism and form primary products of oxidation (hydroperoxides and conjugated dienes). These primary products are unstable and decompose to generate various secondary products, such as aldehydes and ketones (measured as TBARS) [13]. The evolution of the primary lipid oxidation (peroxide index) is shown in Fig. 1. The amount of peroxides gradually decreased during refrigerated storage of liver pâtés due to the decomposition of these compounds into the secondary oxidation products. It is obvious that formation and destruction of peroxides starts during the manufacturing and thermal treatment of pâtés, except for BHT samples. The addition of this synthetic antioxidant (batch B) retarded the beginning of the propagation stage of lipid oxidation. On the other hand, peroxide index was not different ($P>0.05$) among the remaining three batches (A, C and D) at day 0.

TBARS values of pâtés were not affected by refrigerated storage ($P>0.05$). This fact could be due to the particular conditions of conservation of pâtés (vacuum packaging in glass containers, darkness and refrigeration temperature) which limit the oxidation. At day 0, TBARS values of all samples ranged from 0.7 to 5.9 mg MDA/kg of sample, including the BHT samples (primary lipid oxidation delayed). This indicates that the lipid oxidation occurred during the processing of ingredients (scalding of fat and liver) before addition of antioxidants.

Table 1 Evolution of pH, colour parameters, peroxide index and TBARS measured on liver pâtés [A (control), B (BHT, 200 mg/kg), C (tea extract, 200 mg/kg) and D (seaweed extract, 200 mg/kg)] during refrigerated storage (0, 4 and 24 weeks)

		A	B	C	D	*SEM*	*Sig*
pH	Week 0	6.31 ± 0.09	6.25 ± 0.03^{x}	6.21 ± 0.02^{x}	6.19 ± 0.02	0.02	ns
	Week 4	6.30 ± 0.02^{a}	6.16 ± 0.00^{b,y}	6.14 ± 0.00^{b,y}	6.15 ± 0.01^{b}	0.02	**
	Week 24	6.34 ± 0.02^{a}	6.25 ± 0.01^{b,x}	6.22 ± 0.01^{b,x}	6.22 ± 0.01^{b}	0.02	**
	SEM	0.02	0.02	0.02	0.01		
	Sig	ns	*	*	ns		
L*	Week 0	71.89 ± 0.39	71.43 ± 2.16	68.94 ± 2.31	68.86 ± 0.23	0.68	ns
	Week 4	69.34 ± 1.22	68.16 ± 1.73	65.81 ± 0.45	69.38 ± 1.08	0.64	ns
	Week 24	71.39 ± 0.44^{a}	71.39 ± 0.51^{a}	68.43 ± 0.79^{b}	71.11 ± 0.12^{a}	0.49	*
	SEM	0.55	0.86	0.76	0.48		
	Sig	ns	ns	ns	ns		
a*	Week 0	4.36 ± 0.62^{a}	4.17 ± 0.16^{a}	2.28 ± 0.37^{b}	4.08 ± 0.09^{a}	0.33	*
	Week 4	4.43 ± 0.11^{a}	4.36 ± 0.15^{ab}	2.47 ± 0.16^{c}	4.08 ± 0.01^{b}	0.30	***
	Week 24	4.58 ± 0.12^{a}	4.73 ± 0.27^{a}	2.46 ± 0.48^{b}	4.38 ± 0.19^{a}	0.36	**
	SEM	0.12	0.12	0.12	0.07		
	Sig	ns	ns	ns	ns		
b*	Week 0	19.64 ± 0.29^{a,x}	19.65 ± 0.23^{a}	16.03 ± 0.91^{b}	18.92 ± 0.28^{a}	0.58	**
	Week 4	18.78 ± 0.08^{a,y}	19.22 ± 0.11^{b}	15.86 ± 0.23^{c}	18.96 ± 0.16^{ab}	0.52	***
	Week 24	18.35 ± 0.25^{a,y}	18.71 ± 0.30^{a}	15.63 ± 0.64^{b}	18.43 ± 0.49^{a}	0.49	**
	SEM	0.25	0.19	0.22	0.15		
	Sig	*	ns	ns	ns		
Peroxide index (mEq O_2/kg fat)	Week 0	12.02 ± 3.91^{a}	0.00 ± 0.00^{b}	7.68 ± 1.82^{a,x}	10.73 ± 1.53^{a,x}	1.87	*
	Week 4	7.96 ± 0.23^{a}	0.00 ± 0.00^{b}	2.35 ± 1.24^{c,y}	5.82 ± 0.38^{d,y}	1.17	**
	Week 24	3.80 ± 1.80^{a}	0.00 ± 0.00^{b}	0.42 ± 0.00^{b,y}	5.20 ± 0.41^{a,y}	0.87	*
	SEM	1.70	-	1.43	1.15		
	Sig	ns	-	*	*		
TBARS (mg MDA/kg)	Week 0	3.14 ± 0.41^{a}	3.31 ± 0.27^{a}	0.69 ± 0.25^{b}	5.85 ± 0.81^{c}	0.70	**
	Week 4	4.08 ± 0.02^{a}	3.60 ± 0.70^{a}	1.12 ± 0.68^{b}	4.85 ± 0.18^{a}	2.13	**
	Week 24	2.92 ± 0.80^{a}	2.50 ± 0.34^{a}	1.03 ± 0.26^{b}	4.35 ± 0.33^{c}	0.47	*
	SEM	0.28	0.26	0.16	0.32		
	Sig	ns	ns	ns	ns		

$^{a-d}$ Mean values in the same row (different batches on the same storage week) with different letter presented significant differences.
$^{x-y}$ Mean values in the same column (same antioxidant in different weeks) with different letter presented significant differences.
Significance levels: *** (P<0.001), ** (P<0.01), * (P<0.05), ns (not significant, P>0.05).
SEM: standard error of mean.

IV. CONCLUSIONS

In conclusion, only the synthetic antioxidant (BHT) and the tea extract showed a slight antioxidant effect. The first prevented the formation of peroxides during the manufacture of pâté and the second extract showed the lowest TBARS values. However, the addition of the tea extract had a negative effect on the colour of the pâté, fact that could affect to the product acceptability by consumers.

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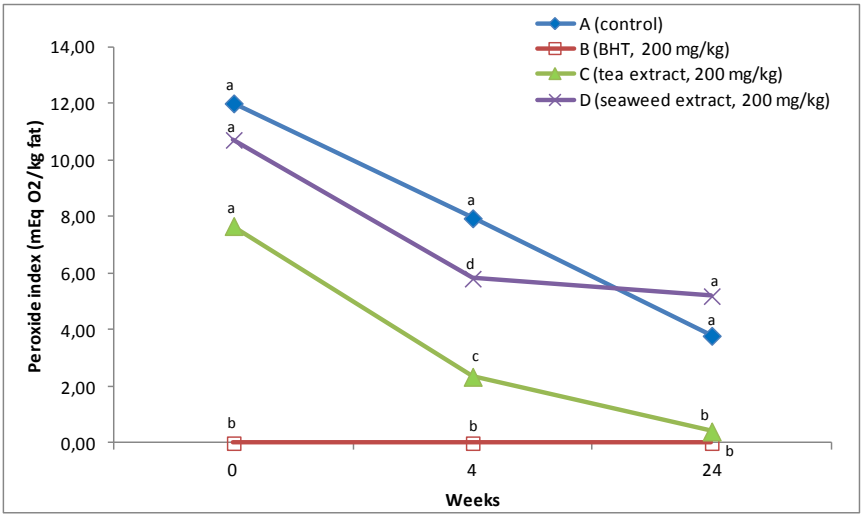

Figure 1 Evolution of peroxide index during refrigerated storage (0, 4 and 24 weeks) of liver pâtés [A (control), B (BHT, 200 mg/kg), C (tea extract, 200 mg/kg) and D (seaweed extract, 200 mg/kg)]. Significant differences ($P<0.05$ for 2 and 24 weeks and $P<0.01$ for 4 weeks) among batches within the same day of storage are denoted by different letters.

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