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INFLUENCE OF THE PH ON OXIDATION OF FROZEN COOKED HAM DURING STORAGE

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Background:

In the recent years, the number of frozen convenience food products on the market has steadily increased. The oxidative stability of these products is often limited by the meat and meat products they contain. A more alkaline pH reduced the oxidative deterioration of meat products [1] and phospholipids [2]. Explanations are either a reduction in the release of trace metal catalysts [3] or of the solubility of transition metals [4]. At alkaline pH the rate of nonenzymatic browning is enhanced [4], oxygen uptake is reduced [5] and decomposition of hydroperoxides catalysed by heme proteins and transition metals is slowed down [6]. However, no similar investigations on frozen cooked ham are available.

Objectives:

The objective of this study was to investigate the effects of alkaline pH on the oxidation of frozen cooked ham by monitoring phospholipid hydroperoxides (PLHP), 2-thiobarbituric acid reactive substances (TBARS), hexanal and sensory evaluation during storage.

Methods

Cooked ham production: Minced (3 mm) pork topside and silverside, and brine (15% by weight relative to meat, preparation with 150 g/kg nitrite curing salt, 40 g/kg dextrose and 5.5 g/kg liquid phosphate; Na_2CO_3 for adjustment of the pH) were tumbled for 90 min (200 mbar, 16 rpm, 2°C). Tumbled meat was stuffed into oxygen-impermeable casings (size 60/70) and cooked at 75°C to a meat core temperature of 68°C. After 12 h at 2°C the hams were cut into 2.5 mm slices and stored in oxygen and light impermeable bags at -10°C under oxygen.

pH measurement: The pH of the cooked hams was measured before slicing using a spear tip electrode. The instrument was calibrated with two buffer solutions of pH 4.001 and 6.865.

TBARS: A previously described [7] and modified [8] method was used as follows. Five ml of steam distillate of homogenised ham (10 g ham + 100 ml distilled water + 1 ml sulphanilamide/N-(1-naphtyl) ethyldiamine solution (v/v) 1:1; pH 1.5) were heated with 5 ml 2-thiobarbituric acid (TBA) solution (100°C; 35 min) and the absorbance was measured at 538 nm. Based on the calibration curve obtained with 1,1,3,3-tetraethoxypropane, TBARS values were expressed in mg malondialdehyde/kg ham. The analysis was performed in duplicate.

Phospholipid Hydroperoxides (PLHP): Using N,N,N′,N′-tetramethyl-1,4-phenylene-diamine hydrochloride as phospholipid-hydroperoxide-specific reagent, the high performance thin layer chromatography (HPTLC) method [9] was performed with 70 µl of Folch extract from 1 g cooked ham. Based on the calibration curve obtained with cumene hydroperoxide (CHP), PLHP were expressed in µg CHP/g ham. The analysis was performed in duplicate.

Hexanal: Ten g ham in 140 ml saturated aqueous NaCl solution and 50 µl 1-decanol were extracted with 4 g CH_2CL_2 for 1 h by SDE (simultaneous distillation extraction) using a Likens-Nickersen apparatus. After addition of 5 µl diphenyl methane as standard, the organic extract was concentrated to 100 µl under nitrogen flow at 25°C. The concentrate was analysed by GC: injection volumne 1 µl; DB Wax column (30 m, ID 0.25 mm, film thickness 0.25 µm, J&W Scientific, Folsom, USA); 5 psi helium at 40°C; temperature program: 20°C for 2 min, from 20°C to 60°C at 40°C min^{-1}, from 60°C to 220°C at 4°C min^{-1} and 220°C for 39 min). Peaks were identified by mass spectrometry.

Sensory evaluation: A multisample rating test was performed according to [10]. A 15-member taste panel described the rancidity using a 10-point scale as follows: not perceived (0-1), slightly perceived (2-3) moderately perceived (4-5), strongly perceived (6-7) and very strongly perceived (8-9). The results shown are averages of the ratings reported by the panellists.

Results and Discussions:

At the beginning of the storage experiments under oxidation-accelerating conditions, no differences were found in PLHP between hams (Figure 1). As the storage went on, PLHP gradually decreased in the control ham, whereas it remained unchanged or even increased in the hams treated with Na_2CO_3. The stability of PLHP seems to be a result of its slower decomposition at higher pH, which is in agreement with previously reported results [2]. In a similar way, as with other meat products, this result could be explained by a smaller release of catalytic iron from histidine residues [3], a lower solubility of transition metals [4] and the reduced catalytic activities of heme proteins and transition metals at higher pH values [6].

Regarding the volatile oxidation markers, TBARS (measured as malondialdehyde, Figure 2) and hexanal (Figure 3) steadiliy increased in the control ham during storage, whereas their increase was slowed down in the hams treated with Na_2CO_3. This result clearly indicates a reduction in the formation of the secondary oxidation by the more alkaline pH of hams. A similar reduction in TBARS was previously reported in meat products at alkaline pH [1].

TBARS and hexanal data correlate well with the data obtained on PLHP, as lipid oxidation is generally accepted to occur stepwise with the formation of primary oxidation products (*e.g.* PLHP) followed by their decomposition into secondary oxidation products (*e.g.* TBARS and hexanal). These analytical results confirmed the importance of phospholipids in oxidation of meat prodcuts [11], which

can readily generate PLHP because of their high amount of polyunsaturated fatty acids [12] especially in phosphatidyl ethanolamine [13]. Moreover, they demonstrate the key role of PLHP in the oxidation process, in particular their decomposition into volatile secondary oxidation products.

The analytical data also correlated well with the sensory results, as demonstrated in Figure 4. The rancid flavour was significantly delayed by carbonate used to adjust the brine to more alkaline pH.

Conclusions:

Results of this work clearly demonstrate a delay in oxidation of the hams at high pH values in the final product. One explanation could be the greater stability of PLHP at higher pH values. A slower decomposition of PLHP reduces the formation of secondary oxidation products and, therefore, improves the quality of the ham during storage. Planar chromatograpy, TBARS and SDE-GC are shown to be suitable tools for the assessment of oxidation in cooked ham. However, it is necessary to confirm the analytical data with sensory evaluation.

Literature:

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Figure 1: PLHP and pH values in cooked hams

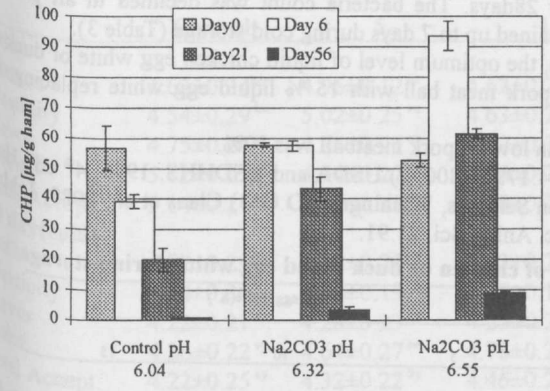

Figure 2: TBARS and pH values in cooked hams

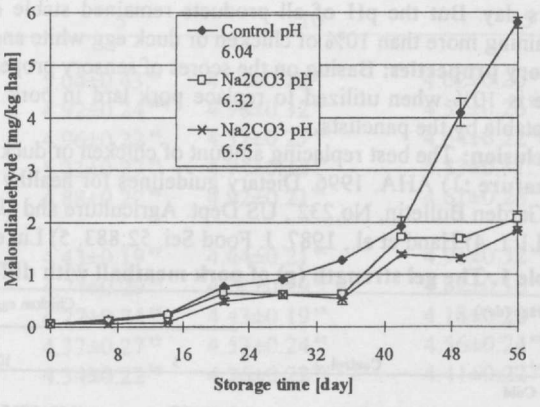

Figure 3: Hexanal and pH values in cooked hams

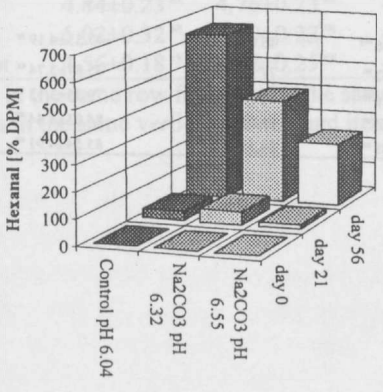

Figure 4: Rancidity score and pH values in cooked hams