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Lability of Collagen in Intermediate Moisture Meat Products

INTRODUCTION

It is well established that, on heating meat in water at temperatures of about 70°C and above increasing amounts of water soluble hydroxyproline containing fragments (gelatins) are produced (e.g. Lawrie, 1979).

Rather more surprisingly Sharp (1963) has shown that following heat treatment, sterile beef and rabbit both yield increasing amounts of hydroxyproline containing water soluble fragments during storage at 37°C. More recently Obanu, Ledward and Lawrie (1975b, 1976) have shown that beef cooked at 100°C, and several different glycerol desorped intermediate moisture meats processed at temperatures of 70°C and above, yield increasing concentrations of soluble hydroxyproline during storage at 38°C. Webster (1980) found that cooked, freeze-dried meat also yielded significant increases in the amount water soluble hydroxyproline during storage at 38°C. No such increases have been observed during the storage of unheated meat samples (Sharp, 1963, Obanu *et al* 1975).

This formation of gelatins, which must arise from degradation of the collagen of the connective tissue of the meat, does lead to significant increases in tenderness (Obanu *et al* 1975b, 1976, Ledward, Lymm and Mitchell, 1981) and obviously could be of tremendous commercial potential in improving the quality of some meat cuts and products prepared from them. As the degradation occurs in sterile, well cooked meat it is unlikely to be due to microbial or enzymic hydrolysis and must therefore arise by one or other chemical reaction(s). Previous work suggests that the degradation occurs far more readily in glycerol desorped meats than in either heated meat of normal moisture content (Obanu *et al*, 1975b) or very low moisture content (Webster, 1980). At the water activity of these glycerol desorped meats ($\sim$ 0.85) lipid oxidation should be optimal and thus the possibility of degradation occurring via interaction with peroxidising lipids seems possible (Zirlin and Karel, 1969). However recent work has shown that glycerol, or rather the traces of aldehydes and peroxides formed in the presence of oxygen, may be responsible for many of the chemically induced changes observed in intermediate moisture meat (Webster, Nunez-Gonzales and and Ledward, 1981). The present work was designed to evaluate the role of glycerol in collagen degradation in intermediate moisture meats.

In addition, the actual amount of heat necessary to make the collagen of meat susceptible to degradation is not known and this was also investigated.

MATERIALS AND METHODS

Preparation and Storage

Beef *longissimus dorsi* trimmed of visible fat and connective tissue was cut into cubes ($\sim 1 cm^3$) and processed to a_w 0.85 in solutions of either glycerol, salt, sorbate and water or salt, sorbate and water only.

The processing was carried out by immersing 140-150 g of meat in 1.5 times its weight of infusing solution (210-225g) in a can. The can was sealed, heated at the appropriate temperature (40 to 100°C) for 70 mins and finally left to achieve complete equilibrium for 18 hours at room temperature (Obanu *et al* 1975a). The infusing solution consisted of either 51% water, 39% glycerol, 9.5% salt and 0.5% potassium sorbate or 70.9% water, 28.6% salt and 0.5% sorbate. These solutions after processing yielded meat of a_w 0.85 $\pm$ 0.2 (Webster, Wood and Ledward, 1979).

Samples were removed from the cans, excess fluid removed by wiping with absorbent tissue and the samples stored, in the presence of air, in Cryovac bags (W.R. Grace Ltd.,) at 38°C as described by Obanu *et al* (1975a). During 15 weeks storage samples were removed for analysis at regular intervals.

Analytical Techniques

Moisture content, pH and percentage soluble hydroxyproline were determined as described by Obanu *et al* (1975a,b).

RESULTS

(a) Effects of glycerol on samples processed at 70°C for 1 hour

During storage at 38°C the moisture content of these samples fell over 12 weeks, from 44.7 to 37.4% in the samples processed in the absence of glycerol and from 45.0 to 37.4% in the samples processed in glycerol. As found in previous studies the pH also fell, from 5.7 to 5.4 over 12 weeks in the presence of glycerol and from 5.7 to 5.2 in the absence of glycerol.

The amount of soluble hydroxyproline in the two samples differed significantly, at all storage times there was significantly more in the samples processed in glycerol (Fig. 1).

(b) Effect of processing temperature

In all these samples there was little loss of moisture during 15 weeks storage at 38°C, the initial content was 45.8% and it decreased by less than 2% irrespective of processing temperature. There was also a drop in pH, from 5.7 to 5.4 in the samples processed at 50°C and above and from 5.7 to 5.3 in those processed at the lower temperatures.

The change in percentage soluble hydroxyproline during storage at 38°C is shown in Figure 2. It is seen that the results fall into one of three patterns. At processing temps of 50°C and below the initial

concentration of soluble hydroxyproline was about 10% and increased only slightly (to about 12%) over 15 weeks storage. At 60 and 65°C the initial concentration of soluble hydroxyproline was higher (12% at 60°C and 19% at 65°C) and it rose to about 30% after 15 weeks (31.5% at 65°C and 27.5% at 60°C). At 70°C and above the initial concentration of soluble hydroxyproline was higher still (33-34%) and after 15 weeks increased to 43-44% in the samples processed at 70 and 80°C and to about 50% in the samples processed at 100°C.

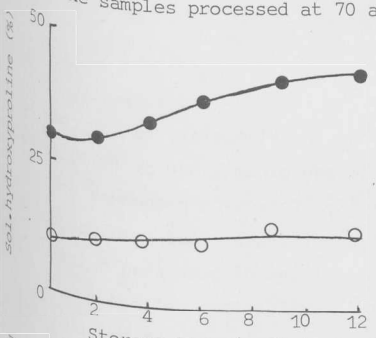

Fig. 1. Increase in soluble hydroxyproline in i.m. beef of a 0.85 desorped in glycerol-salt solution(●)and salt(○) solutions during storage at 38°C.

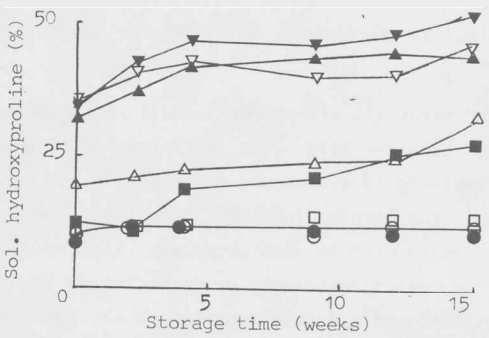

Fig. 2. Effect of processing temperature (○, 40°C, ●, 45°C, □, 50°C, ■, 60°C, △, 65°C, ▲ 70°C, ▽, 80°C, ▼, 100°C) on the formation of soluble hydroxyproline in glycerol-salt desorped beef stored at 38°C.

DISCUSSION

It is readily apparent from Figure 1 that, although significant increases in the amount of soluble hydroxyproline occurs in the absence of glycerol, the presence of glycerol markedly increases the rate and extent of collagen degradation. It may be that the glycerol is merely acting as an inert diluent and, as such, is increasing the rate of reaction by increasing the volume and viscosity of the liquid phase. However it has been observed that in the presence of glycerol the rate of several deteriorative reactions occurring in intermediate moisture foods of a$_w$ 0.85 are decreased (Warmbier, Schnickels and Labuza, 1976). Thus it seems likely that the increased rate of collagen degradation observed in the presence of glycerol is due to it acting merely as a inert diluent. Recently Webster et al (1981) and Obanu et al (1977) have suggested that glycerol, or rather its oxidation products, can take part in chemical reactions in intermediate moisture foods. It seems likely therefore that these reactions are major contributors to the degradation of collagen in these meats. However this degradation also occurs, albeit for more slowly, in full moisture and freeze-dried cooked meats and in these cases glycerol oxidation products can not be responsible. Peroxidising lipids though are known to be capable of degrading proteins (Zirlin and Karel, 1969) and thus these may be the reactants responsible for collagen degradation in glycerol free meats.

Whatever the cause of the degradation it is apparent from Figure 2 that only at temperatures of 60°C and above is the breakdown appreciable. It is well established that the collagen of intra-muscular connective tissue denatures in the range 57 to 61°C (Chizzolini, Ledward and Lawrie, 1976) and separate experiments (not reported here) have shown that in both infusing solutions the denaturation temperature of the connective tissue collagens are similar to the values found in water being about 1°C less in the infusing solution containing glycerol and about 4°C less in the solution containing glycerol. Thus it would appear that the collagen needs to be in the denatured form to be amenable to degradation.

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