PHOTOOXIDATION OF MEAT PIGMENTS.

WAVELENGTH DEPENDENCE ON PIGMENT OXIDATION INVESTIGATED IN MODEL SYSTEMS AND UNDER STORAGE CONDITIONS.

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INTRODUCTION

The colour of meat products is largely determined by the relative amounts of different muscle heme pigments. The pigments in nitrite cured products are nitrosylmyoglobin (NOMb) and metmyoglobin (MMb), while the pigments in fresh and frozen meat products are myoglobin (Mb), oxymyoglobin (MbO_2) and MMb. The change in colour from bright red to gray and brown hues for nitrite cured meat products and from cherryred to brown for fresh and frozen meat products, both unacceptable to the consumer (Walters, 1974, Hood and Riordan, 1973) are primarily due to oxidation of NOMb to MMb, and of MbO_2 to MMb, respectively. However the rates by which these oxidation processes proceed, and thereby the rates of product discoloration, depend on a wide variety of factors including product pH, the nature and concentration of additives, storage temperature and the wavelength distribution and intensity of light used for display in combination with the light permeability of the packaging material. Although the problem of light induced discoloration of meat products during display is becoming generally recognized, the photochemistry behind this important phenomenon is poorly understood, especially in connection with other deteriorative processes in meat products. Accordingly, we have investigated the wavelength dependence on photooxidation of NOMb and MbO_2 in aqueous model systems, and the applicability of the results from these model experiments to practical storage in the retail trade was subsequently tested in experiments with meat products displayed in illuminated cabinets. Packaging material with and without UV-light absorber incorporated was tested in order to aid the difficult process of optimizing packaging conditions for meat products.

MATERIALS AND METHODS

Chemical experiments

Myoglobin derivatives: NOMb and MbO_2 were syntesized from equine MMb (Sigma type III) according to Andersen and Skibsted (1989) and Andersen et al. (1988b).

Kinetic experiments: Pre-thermostatted solutions of equine NOMb or MbO_2 were mixed with phosphate buffer solution at pH 5.5 to give an appropriate absorbance and a total buffer concentration of 0.020 M, and the ionic strength was adjusted with NaCl (analytical grade) to 0.16 (physiological concentration). The rate of autoxidation was measured spectrophotometrically (450 to 650 nm, corresponding to the absorption in the visible range). The data presented in this communication as rate of autoxidation for MbO_2 and NOMb under conditions relevant for meat products have also formed the basis for detailed kinetic analysis involving transition state theory as described elsewhere (Andersen et al., 1988b, Andersen and Skibsted, 1989).

Continuous wave photolysis: The photolysis solutions (NOMb or MbO_2 solutions) were irradiated with monochromatic light under conditions similar to those employed for the kinetic experiments, and the rate of

photooxidation was monitored spectrophotometrically. The methods used in the continuous wave photolysis and the transformation of the rate data to reaction quantum yields are described in detail elsewhere (Bertelsen and Skibsted, 1987; Andersen and Skibsted, 1989).

Storage experiments

The storage experiments reported here are part of other investigations performed with different purposes and described in detail elsewhere (Andersen et al. 1988a,1989).

Product and packaging: Canned pasteurized ham (5% fat, 18% protein, 26.5% dry matter) containing 60 ppm nitrite, 350 ppm ascorbic acid and 3% sodium chloride was supplied by a meat processing plant. After slicing (16x10x0.16 cm) it was randomly packed (two slices per pouch) using packaging materials with an oxygen transmission rate (OTR) < 4 $cm^3/m^2/24h/atm$ (25 °C, r.h. 75%) and an initial vacuum level of 99%. Two packaging materials were used, one with an UV-light absorber incorporated which excludes a large amount of light beneath 360 nm, and one fully transparent to UV-light (Schur-Pack International Inc., DK-8700 Horsens).

Beef from forequarters of traditionally slaughtered cattle was mixed with salt (1%), texturized soy protein (4%), and water (14%) and was ground through a 70% 0.3 cm plate. The resulting minced beef product (1.1% salt, 13% fat, 19% protein, pH = 6.0, as analyzed by standard methods) was packed in 400 g portions in polyethylene tubes with and without UV-light absorber incorporated, and with an OTR of ca. 1000 $cm^3/m^2/24h/atm$ (25 °C, r.h.75%).

Storage: The vacuum-packed, sliced ham was placed in the upper layer of an illuminated chill cabinet (gondola, with forced air circulation). At the surface of the product the temperature was approximately 8 °C; however, during the daily defrosting, the temperature rose to approximately 12 °C. Each of the displayed packs was partially covered with black plastic, allowing direct comparison during storage of the colour of products exposed to light and products protected from light.

After freezing at -24 °C in a freezer storage room for 12 hours the minced beef was placed in the upper section of a freezing cabinet (gondola with forced air circulation) illuminated by fluorescent tubes. The product temperature was approximately -18 °C; however, during daily defrosting, the product temperature rose to approximately -12 °C. Like the vacuum-packed ham, each of the displayed packs was partially covered with black plastic.

Light sources: Fluorescent tubes (Philips TLD 18W/36) were used for illumination in both storage experiments, giving an illuminance of 600 lx on the surface of the vacuum-packed ham, where a radiant flux density of UV-light (300-400 nm) of ca. 40 mW/m^2 was measured, and an illuminance of 520 lx on the surface of the frozen beef product, where a radiant flux density of UV-light (300-400 nm) of ca. 21 mW/m^2 was measured.

Colour measurement: The surface colour of the vacuum-packed ham and of the frozen minced beef was measured with a tristimulus colorimeter (HunterLab D-25 equipped with a D25 optical sensory head) standardized against a white standard with L=90.7, a= -0.9, and b=-0.1.

RESULTS

Chemical experiments

In Fig. 1, the relative rates of photooxidation of NOMb and MbO_2 resulting from monochromatic light of wavelengths of particular abundance in fluorescent light are compared to the rate of thermal oxidation for MbO_2 and NOMb, respectively. The rate of thermal oxidation is based on activation parameters derived from the kinetics experiments for each of the pigments, and for the light-induced oxidation, the rate is based on the initial photooxidation yields (up to 20% conversion). For the light-induced oxidation rates a slight temperature dependence contrasts, at the given pH, the remarkably high energies of activation for thermal NOMb and MbO_2 autoxidation, as may be seen in Fig. 1. For temperature and light intensity conditions relevant for meat display, light-induced oxidation of NOMb is at least an order of magnitude faster than the thermal autoxidation at the surface of the product. This is in contrast to thermal MbO_2 autoxidation for which the photooxidation only below a certain temperature, depending on the wavelength distribution of the light, exceeds the thermal autoxidation.

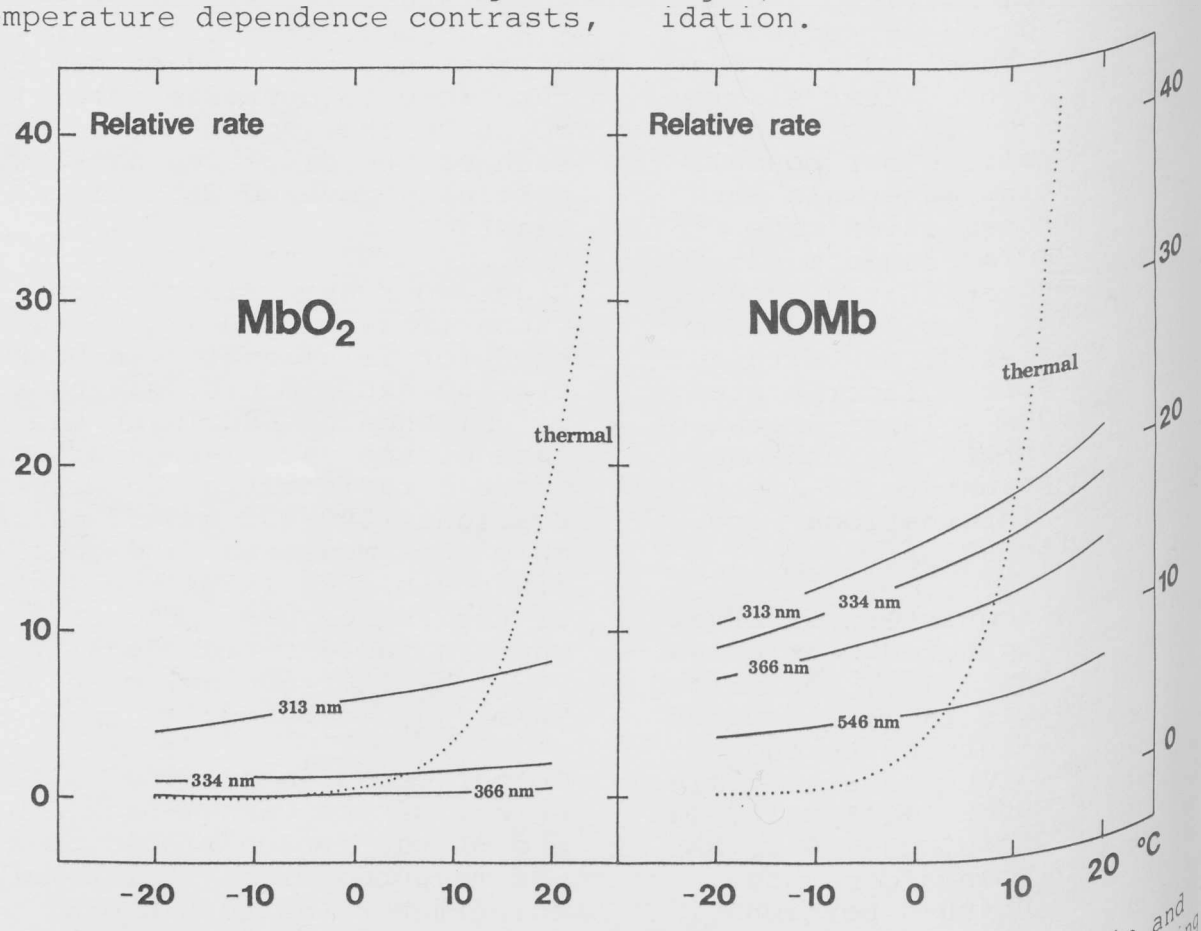

Fig. 1. Thermal and light-induced autoxidation of oxymyoglobin and nitrosylmyoglobin under conditions relevant for meat products during display in the retail trade. The rate is determined for aqueous solutions of MbO_2 and NOMb with pH = 5.5, illuminated by monochromatic light with wavelengths of particular intensity in fluorescent light ($5\ mW \cdot ml^{-1}$ used for the calculation).

Storage experiments

Among the tristimulus parameters L, a, and b, the redness parameter Hunter a was found to yield the best correlation with the subjective colour score of the actual products (Andersen et al., 1988a). In order to minimize interference from packaging material and from inhomogeneity of the products, the Hunter a parameter was normalized relative to its initial value and Δa, the change in redness (Δa(t) = a(t) - a(t = 0), is used in the presentation of colour changes during storage.

For vacuum-packed, sliced ham, light had a significan effect on the surface discoloration of the product (Fig. 2, which shows the fading red colour expressed as Δa). However, the UV-barrier had little, if any, protecting effect under the actual storage conditions.

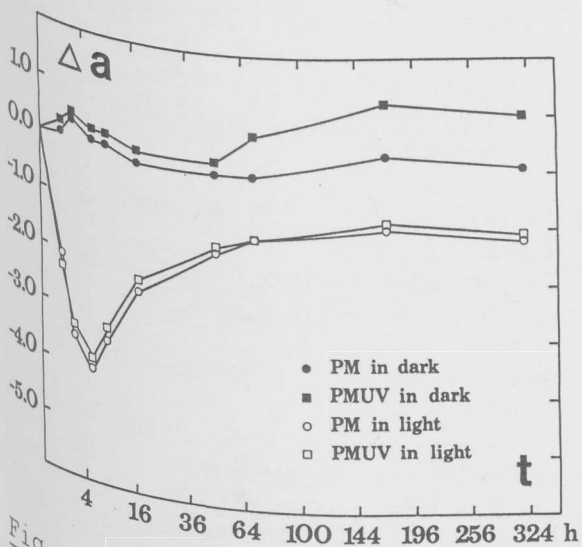

Fig. 2. Fading of red colour (measured as change in Hunter a value) during storage of sliced, vacuum-packed ham displayed in a chill cabinet: Effect of fluorescent light and UV-light permeability. PM denotes a packaging material transparent to light in the UV-region, whereas PMUV denotes a packaging material with a UV-barrier excluding light below 360 nm.

The effect of light on the discoloration process of frozen minced beef may be inferred from Fig. 3, which shows the gradual change in redness, for frozen minced beef packed in polyethylene with and without UV-light barrier. For the frozen product packed in normal polyethylene, exposure to light clearly accelerates discoloration. Notably, the same product packed in polyethylene with a UV-light barrier has almost the same colour stability as the product stored in the dark.

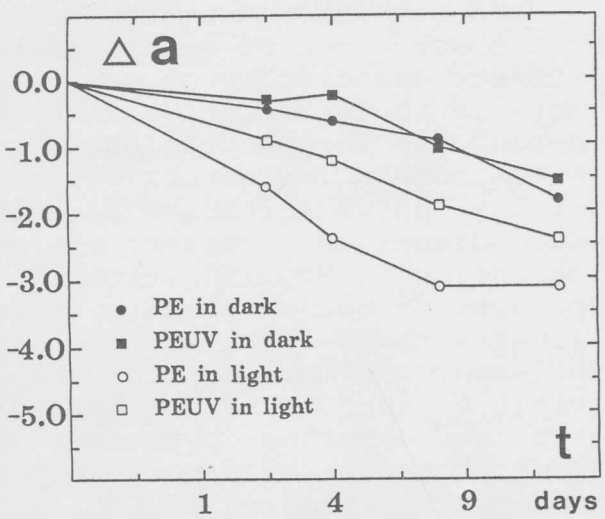

Fig. 3. Surface discoloration (measured as change in Hunter a value) during storage of frozen, minced beef in a freezer cabinet. Effect of fluorescent light and UV-light permeability. PE denotes normal polyethylene, whereas PEUV denotes polyethylene with a UV-barrier excluding light below 360 nm. Figure is modified after Andersen et al., 1989.

CONCLUSION

In the presence of oxygen, the photooxidation of NOMb is faster than the photooxidation of MbO_2. This result has been found for aqueous solution model systems with monochromatic light (Fig.1). Accordingly, the colour of ham was expected to be more sensitive to light than the colour of fresh and frozen meat. This prediction was confirmed in practical storage experiments (Figs. 2 and 3), and it was found that the rate of discoloration is significantly faster for ham than for frozen beef as long as oxygen is present in the vacuum-packed product. Another important observation of relevance to storage and display of meat products is the different wavelength dependence for photooxidation of NOMb and MbO_2. Photooxidation of NOMb shows little wavelength dependence; in contrast, photooxidation of MbO_2 is strongly dependent on the wavelength of the light with UV-light being orders of magnitude more harmful than visible light. UV-light barriers are thus expected to protect beef stored below a certain temperature (depending on the light intensity), but to yield only little protection for ham. This prediction was fully confirmed in the storage experiment (Figs. 2 and 3).

The predictive power of the results obtained in aqueous solution model systems to the colour stability during practical storage of meat products has been rather encouraging, and we are currently using the same experimental strategy in investigations of the influence of salt and product pH in combination with light on general oxidative stability of meat products.

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REFERENCES

Andersen, H.J., Bertelsen, G., Boegh-Soerensen, L., Shek, C.K. & Skibsted, L.H.(1988a): Effect of Light and Packaging Conditions on the Colour Stability of Sliced Ham. Meat Sci. 22, 283.

Andersen, H.J., Bertelsen, G. & Skibsted, L.H. (1988b): Salt Effect on Acid-Catalyzed Autoxidation of Oxymyoglobin. Acta Chem. Scand. A, 42, 226.

Andersen, H.J., Bertelsen, G. & Skibsted, L.H. (1989): Colour Stability of Minced Beef. Ultraviolet Barrier in Packaging Material Reduces Light-Induced Discoloration of Frozen Products during Display. Meat Sci. 25. In press.

Andersen, H.J. & Skibsted, L.H. (1989): Photooxidation of Nitrosylmyoglobin. In preparation.

Bertelsen, G. & Skibsted, L.H. (1987): Photooxidation of Oxymyoglobin. Wavelength Dependence of Quantum Yields in Relation to Light Discoloration of Meat. Meat Sci. 19, 243.

Hood, D.F. & Riordan, E.B.(1973) Discoloration in pre-packaged Beef. J. Food Technol. 8, 333.

Walters, C.L. (1974): Meat Colour: The Importance of Haem Chemistry. In: Meat, by Cole, D.J.A. and Lowrie, R.A. (ed.). Butterworth, p. 385.