



Review

Myoglobin and lipid oxidation interactions: Mechanistic bases and control

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ABSTRACT

Lipid oxidation and myoglobin oxidation in meat lead to off-flavor development and discoloration, respectively. These processes often appear to be linked and the oxidation of one of these leads to the formation of chemical species that can exacerbate oxidation of the other. Several investigators have reported preservation of fresh meat color following the inclusion of antioxidant ingredients. An understanding of the complementary oxidation interaction provides a basis for explaining quality deterioration in meat and also for developing strategies to maintain optimal sensory qualities.

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1. Introduction

Sensory properties of meat contribute significantly to the perception of quality and value, and this is especially true for the color of meat. Meat discoloration compromises its appearance and is due to the conversion of oxymyoglobin (OxyMb) to metmyoglobin (MetMb). This change results from a decrease in heme redox stability rather than the oxidation of specific amino acid residues. The oxidation of unsaturated fatty acids in phospholipids and triacylglycerols, hereafter referred to as lipid oxidation, contributes to off-flavors. The biochemical reactions directly responsible for myoglobin oxidation and lipid oxidation each generate products that can further accelerate oxidation in a reciprocal manner. Greene and colleagues (Greene, 1969; Greene, Hsin, & Zipser, 1971) were among the first

meat scientists to document the concurrent increase in lipid oxidation and discoloration in meat. Significant support for an interaction between the processes of lipid oxidation and discoloration has been provided by antioxidant mediation of both processes. For example, it was known for many years that the lipid-soluble antioxidant, α -tocopherol, delayed lipid oxidation in meat from various livestock species (Faustman, 2004). However, the observation that α -tocopherol also delayed beef discoloration, a process based on oxidation of a water-soluble protein, provided evidence for a strong link between these processes. Chaijan (2008) recently reviewed the relevance of this oxidative interaction to muscle foods. This reference should be consulted for a more extensive discussion of the classical steps of lipid oxidation (i.e., initiation, propagation and termination) and of the production of reactive oxygen species from ferrous OxyMb oxidation. The objective of our review is to elucidate the potential mechanisms by which this oxidative interaction may occur and provide examples of its practical significance to fresh muscle foods of mammalian origin.

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2. Lipid oxidation

The process of lipid oxidation has been reviewed extensively in the meat and food science literature (Decker & Xu, 1998; Faustman, Naveena, Yin, & Tatiyaborworntham, 2010; Monahan, 2000). Substrates necessary for this deteriorative reaction include unsaturated fatty acids, oxygen and chemical species that accelerate oxidation (e.g., iron; Kanner, Shegalovich, Harel, & Hazan, 1988); these are abundant in meat displayed aerobically or in high-oxygen modified atmosphere packaging. A variety of intrinsic properties and processing steps can predispose meat to lipid oxidation. For example, meat from non-ruminants contains greater relative concentrations of unsaturated fatty acids within triacylglycerols (Enser, Hallett, Hewett, Furse, & Wood, 1996) and generally displays more rapid lipid oxidation than that of ruminants (Tichivangana & Morrissey, 1985); muscles with greater proportions of red fibers are susceptible because they contain more iron and phospholipid than muscles containing predominantly white fibers (Wood et al., 2004); ground meat experiences greater lipid oxidation than whole cuts because the grinding process incorporates oxygen, mixes reactive components, and increases surface area as a result of particle size reduction (Gray, Goma, & Buckley, 1996). The fortification of meat products with n-3 polyunsaturated fatty acids to improve its nutritional profile adds susceptible substrate (Apple, Maxwell, Galloway, Hamilton, & Yancey, 2009) that requires antioxidant approaches for minimizing oxidation (Lee, Faustman, Djordjevic, Faraji, & Decker, 2006).

Several products of lipid oxidation are responsible for rancid odors and flavors, and some are very reactive. Primary products of lipid oxidation include chemical species formed during the initiation and early propagation steps. Alkyl, alkoxy and peroxy radicals may all be produced and readily abstract protons from neighboring molecules. Peroxides are commonly formed as primary products and can subsequently undergo scission to form lower molecular-weight secondary oxidation products including aldehydes, ketones and epoxides. Specific and well known examples of these include hexanal, propanal, malondialdehyde (Sakai, Yamauchi, Kuwazuru, & Gotoh, 1998; Siu & Draper, 1978) and 4-hydroxynonenal (Sakai, Kuwazuru, Yamauchi, & Uchida, 1995). Park, Kim, Lee, Yoo, Shim, and Chin (2008) recently characterized several volatile and non-volatile products of lipid oxidation in pork belly and loin.

3. Myoglobin oxidation

Myoglobin is the heme protein responsible for meat color. The oxidation of the central iron atom within the heme group is responsible for discoloration, a change from red OxyMb to brownish MetMb. When ferrous heme iron oxidizes to its ferric form, oxygen is released and replaced by a water molecule.

There has been substantial debate in the literature as to whether the rate of OxyMb oxidation or the rate of MetMb reduction is the predominant determinant of meat color stability (Ledward, 1985; O'Keefe & Hood, 1982). However, the purpose of this review is to focus on OxyMb oxidation and its contribution to meat discoloration. The rate of discoloration in meat is muscle-specific (Jeong et al., 2009; McKenna et al., 2005; O'Keefe & Hood, 1982). Muscles that contain greater relative proportions of red fibers, and thus more lipid and greater oxygen consumption rates, appear to discolor more quickly.

Many factors affect OxyMb oxidation (Faustman & Cassens, 1990; Renner, 2000). These include temperature, pH, MetMb reducing activity, partial oxygen pressure and lipid oxidation. OxyMb oxidation is favored by higher temperatures (Brown & Mebine, 1969), lower pH values (Gotoh & Shikama, 1974) and the presence of non-heme iron (Allen & Cornforth, 2006). MetMb reducing activity can be enzymically or non-enzymically based and favors maintenance of ferrous forms of myoglobin in meat (Bekhit, Simmons, & Faustman,

2005). Partial oxygen pressures (pO_2) in which a complete vacuum exists or in which oxygen saturation is attained favor ferrous myoglobin forms. Low non-zero pO_2 favors MetMb formation (George & Stratman, 1952; Ledward, 1970; Neill & Hastings, 1925). Lipid oxidation appears to enhance OxyMb oxidation and is discussed below.

4. Lipid oxidation as a facilitator of myoglobin oxidation

Several studies have reported that the process of lipid oxidation enhances meat discoloration. Zakrys, Hogan, O'Sullivan, Allen, and Kerry (2008) recently investigated quality parameters in beef packaged under 0%, 10%, 20%, 50% and 80% oxygen (20% CO_2 , balance nitrogen). They concluded that "changes in OxyMb and a^* values appeared to be driven by lipid oxidation and correlated strongly with TBARS". The mechanisms by which lipid oxidation could enhance myoglobin oxidation have been explained primarily on the reactivity of primary and secondary products derived from unsaturated fatty acids. Supplementation of livestock with diets enriched in polyunsaturated fatty acids leads to the meat subsequently obtained from these animals being more susceptible to lipid oxidation and discoloration (Nute et al., 2007). McKenna et al. (2005) reported on the relationship between several endogenous factors that affect beef color stability. Muscles with greater color stability were characterized by less oxygen consumption and less lipid oxidation. O'Grady, Monahan, and Brunton (2001) utilized model systems and demonstrated a role for lipid oxidation in myoglobin oxidation. Muscle microsomes with greater degrees of fatty acid unsaturation promoted greater OxyMb oxidation in vitro (Yin & Faustman, 1994).

Incubation of specific products of lipid oxidation (e.g., α,β unsaturated aldehydes; Grimsrud, Xie, Griffin, & Bernlohr, 2008) with OxyMb (Faustman, Liebler, McClure, & Sun, 1999) increases MetMb formation. 4-Hydroxynonenal is a secondary product of n-6 fatty acid oxidation (Pryor & Porter, 1990) that is very reactive and has received considerable attention in the medical (Poli, Schaur, Siems, & Leonarduzzi, 2007) and food science literature (Surh & Kwon, 2005; Surh, Lee, & Kwon, 2007). HNE has been identified in meat (Table 1; Sakai et al., 1998) and its formation is favored by freeze-drying (Gase et al., 2007). Pre-incubation of MetMb with HNE rendered it a poorer substrate for enzymatic MetMb reduction than untreated MetMb (Lynch & Faustman, 2000). Garry and Mammen (2007) recently noted that one of myoglobin's functions in vivo is to serve as a scavenger of reactive oxygen species.

5. Myoglobin as a facilitator of lipid oxidation

The role of heme proteins in general, and myoglobin specifically, in enhancing lipid oxidation has been studied extensively. Considerable debate in the literature has focused on the relative contributions of heme and non-heme iron to lipid oxidation in meat (Baron & Andersen, 2002; Carlsen, Moller, & Skibsted, 2005; Love, 1983; Younathan & Watts, 1959). Greater concentrations of iron and myoglobin are associated with greater rates of lipid oxidation (Faustman,

Table 1

Changes in HNE content and TBARS values of pork stored at 0 °C (adapted from Sakai, Yamauchi, Kuwazuru and Gotoh, 1998).

	Days of storage			
	0	3	7	12
HNE (nmol/g meat)	6.03 ± 1.39 ^a	7.03 ± 2.04 ^a	7.42 ± 1.88 ^a	27.96 ± 5.59 ^b
TBARS (nmol MDA/g meat)	0.19 ± 0.01 ^a	0.39 ± 0.03 ^{ab}	0.83 ± 0.12 ^b	3.08 ± 0.28 ^c

Each value is the mean ($n=3$) ± standard deviation. Values in rows with different superscripts are different ($P<0.05$).

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