Antioxidants INMuscle Foods

NUTRITIONAL STRATEGIES
TO IMPROVE QUALITY

Edited by
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ANTIOXIDANTS IN MUSCLE FOODS

Nutritional Strategies to Improve Quality

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PREFACE

The use of nutritional strategies to improve the quality of food products from livestock and fish is a relatively new approach that has emerged at the interface of animal science and food science.

Improvement of Oxidative Stability of Beef and

These strategies for obtaining muscle-based foods of superior quality have emphasized alteration of nutritional profile (e.g., increased content of polyunsaturated fatty acids), improved pigmentation (e.g., carotenoid supplementation of salmonids to obtain desirable flesh color), and improved oxidative stability (e.g., supplementation of cattle with vitamin E to minimize pigment and lipid oxidation in beef). Interestingly, these approaches carry with them additional benefits and concerns. For example, pork with elevated concentrations of α -tocopherol is less susceptible to formation of potentially toxic cholesterol oxidation products. In addition to their pigmenting ability, carotenoids may also display some antioxidant behavior. Also, muscle foods are generally low in antioxidant nutrients and dietary supplementation for purposes of sensory quality issues may also improve the antioxidant nutrient profile of these products.

Nutritional approaches to improve the oxidative quality of muscle foods are often more effective than direct addition of food ingredients since the antioxidant is preferentially deposited where it is most needed (e.g., α -tocopherol incorporation into lipid membrane systems). In addition, diet often represents the only technology available to alter the oxidative stability of intact muscle foods (e.g., steaks and roasts), where utilization of exogenous antioxidant additives is difficult if not impossible. Since product composition is altered biologically, nutritional alteration of muscle composition is more label-friendly since no additive declarations are required.

The purpose of this book is to examine dietary approaches for improving the quality of muscle-based foods. Specifically, we emphasize the oxidative quality of these food products since progress has been most evident in this area. The book is organized in three sections beginning with the scientific bases for oxidative reactions common to muscle foods, followed by dietary strategies used to influence the antioxidant composition of muscle, and finally the scientific and economic implications of muscle foods with altered composition.

As noted previously, the connection between the animal and food sciences has not been well developed. We hope that documentation of improved muscle food quality

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as described herein will stimulate additional thought and investigation for further utilizing dietary approaches for this outcome.

would not have met to share research results and discuss issues central to the theme of

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OXIDATIVE PROCESSES IN MUSCLE FOODS

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CHAPTER 1

Oxidation of Lipids in Muscle Foods: Fundamental and Applied Concerns

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Consecutive One Electron Reduction of O. Consecutive one-electron reduction of molecular oxygen to water results HOITAGIXO; GIRLING WATERMENTO superoxide, hydrogen permit of, and the hydroxyl radical.

Lipid exidation is the process by which molecular oxygen reacts with uscalurated lipids to form lipid peroxides. The direct renction of lipids with oxygen is spin-folyidden because the ground state of lipids is of singlet multiplicity whereas oxygen is of triplet multiplicity. However, the spin extriction can be exercisme by initiators or musture variables such as temperature, physiological reduction of oxygen to water, photosensities, radiation, singlet oxygen, oxygen-transition inortheres, or by enzymic throwy general likely cambysis. Lipid exidation is known to proceed by a free radical chain reaction mechanism involving initiation, propagation/branching, and termina-

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Oxidation of Lipids in Muscle Foods: Fundamental and Applied Concerns

FRANK J. MONAHAN

INTRODUCTION

Oxidation of lipids is a reaction of major significance in all living tissues and has both beneficial and detrimental consequences for the well-being of living organisms (Sevanian and Hochstein, 1985). In muscle-derived foods the fine control mechanisms that exist to control lipid oxidation reactions in vivo are much less effective and lipid oxidation proceeds in a comparatively uncontrolled manner (Sies, 1986). While lipid oxidation reactions contribute to certain positive quality attributes, such as the development of desirable flavors in cooked meats (Farmer, 1992), the overall effect of lipid oxidation is negative and lipid oxidation over time has adverse effects on color, odor, flavor, and healthiness of meat products (Pearson et al., 1983; Gray and Pearson, 1987).

CHEMISTRY OF LIPID OXIDATION

Lipid oxidation is the process by which molecular oxygen reacts with unsaturated lipids to form lipid peroxides. The direct reaction of lipids with oxygen is spin-forbidden because the ground state of lipids is of singlet multiplicity whereas oxygen is of triplet multiplicity. However, the spin restriction can be overcome by initiators or initiating variables such as temperature, physiological reduction of oxygen to water, photosensitizers, radiation, singlet oxygen, oxygen-transition metal complexes, or by enzymic (lipoxygenase-like) catalysis. Lipid oxidation is known to proceed by a free radical chain reaction mechanism involving initiation, propagation/branching, and termination stages.

Initiation 1

 $LH + Initiator \rightarrow L^{\bullet}$

Propagation $L^{\bullet} + O_2 \rightarrow LOO^{\bullet}$

LOO° + LH → LOOH + L°

Branching $LOOH \rightarrow LO^{\bullet} + OH^{\bullet}$ $2LOOH \rightarrow LOO^{\bullet} + LO^{\bullet} + H_2O$ Termination $LOO^{\bullet} + LOO^{\bullet} \rightarrow LOOL + O_2$ $LOO^{\bullet} + L^{\bullet} \rightarrow LOOL$ $L^{\bullet} + L^{\bullet} \rightarrow LL$ $L^{\bullet} (LOO^{\bullet}, LO^{\bullet}, OH^{\bullet}) + AH \rightarrow LH (LOOH, LOH, H_2O) + A^{\bullet}$

Initiation occurs when a hydrogen atom is abstracted from a fatty acid molecule (LH) to form a lipid radical (L*). Propagation involves the reaction of the lipid radical (L*) with molecular oxygen to form a lipid peroxy radical (LOO*). The lipid peroxy radical can abstract a hydrogen atom from another unsaturated fatty acid and propagate the chain reaction. The lipid hydroperoxides (LOOH) formed may undergo homolytic scission to form alkoxyl (LO*) and hydroxyl radicals (OH*), which are capable of propagating further oxidation and lead to chain branching. Termination involves the reaction of free radicals to form noninitiating and nonpropagating products. Chain-breaking antioxidants (AH) terminate the free radical chain reaction by donating hydrogen atoms to free radical species and forming less reactive products.

Initiators of Lipid Oxidation

Lipid oxidation involving ground state oxygen proceeds very slowly without the aid of initiators (Rawls and Van Santen, 1970; Frankel, 1985). There are several ways of overcoming the spin restriction and allowing the reaction of oxygen with lipids and other biological substrates (Table 1-1).

Consecutive One-Electron Reduction of O_2 Consecutive one-electron reduction of molecular oxygen to water results in the formation of three intermediates: superoxide, hydrogen peroxide, and the hydroxyl radical.

$$O_2 + e \rightarrow O_2^{\bullet -}$$

$$O_2^{\bullet -} + e + 2H^+ \rightarrow H_2O_2$$

$$H_2O_2 + e + H^+ \rightarrow OH^{\bullet} + H_2O$$

$$OH^{\bullet} + e + H^+ \rightarrow H_2O$$

In muscle foods superoxide $(O_2^{\bullet-})$ could arise from membranal electron transfer systems, autoxidation of oxymyoglobin to metmyoglobin, oxidase activity, activation of leukocytes present in the vasculature of muscle tissue, or oxidation of ascorbic acid and other reducing components by iron (Kanner et al., 1987). The loss of charge following protonation of $O_2^{\bullet-}$ should permit the perhydroxyl radical formed (HO_2^{\bullet}) to penetrate lipid membranes and initiate lipid oxidation. However, based on its pKa (4.8) under physiological conditions, this activated oxygen species exists as an anion with its radical activity suppressed (Gebicki and Bielski, 1981). Despite the fact that

TABLE 1-1 Proposed Initiators of Lipid Oxidation in Muscle

Singlet oxygen
Superoxide radical
Hydroxyl radical
Ferryl radical
Perferryl radical
Ferrous-dioxygen-ferric complex
Hydrogen peroxide—activated metmyoglobin

Source: Adapted from Asghar et al., 1988.

proportionately more superoxide would exist in the protonated form at the postmortem pH of muscle (5.5–6.0) than at physiological pH, superoxide is not believed to contribute directly to the initiation of membranal lipid peroxidation.

Hydrogén peroxide (H_2O_2) is the second intermediate of oxygen reduction and can arise from both superoxide dismutase-catalyzed dismutation and nonenzymic dismutation of superoxide. In addition, H_2O_2 can be generated directly by enzymes such as aldehyde oxidase and glucose oxidase (Kanner et al., 1987) or the autoxidation of flavins, thiols, and phenoleates (Kanner et al., 1986). In the absence of heavy metal ions, energy-rich radiation, or elevated temperatures, H_2O_2 has limited reactivity. However, one-electron reduction of H_2O_2 gives rise to the hydroxyl radical, which is highly reactive. Decomposition of H_2O_2 to OH^- and OH^{\bullet} occurs in the presence of Fe^{2+} by the Fenton reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$$

The presence of H_2O_2 in muscle tissue postmortem, and of transition metals that promote its breakdown to OH^{\bullet} , make the OH^{\bullet} radical a likely initiator of lipid oxidation in muscle foods. Hydroxyl radicals can also be readily formed in superoxide-generating systems in the presence of iron or copper salts by the Haber–Weiss mechanism.

$$Fe^{3+} + O_2^{\bullet-} \rightarrow Fe^{2+} + O_2$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$

$$Net: O_2^{\bullet-} + H_2O_2 \rightarrow O_2 + OH^{\bullet} + OH^{-}$$

Formation of Singlet Oxygen in Excited State Oxygen goes from the triplet ground state ${}^3\Sigma_g$ to the singlet state by the uptake of energy; there are two excited states of singlet oxygen and the lower of these, the ${}^1\Delta_g$ state, is sufficiently stable to engage in reactions in solution. Singlet oxygen, ${}^1\Delta_g$, is electrophilic, the spin restriction