

Do phospholipolysis and bacteria primarily regulate linoleic acid oxidation in fresh meats?

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Abstract. The release of polyunsaturated fatty acids (PUFA) from cell membranes by phospholipolysis followed by (per)oxidation, is the major integrated process in the oxidative spoilage of meat. Only free PUFAs are susceptible to oxidation. Rancid meat is an excellent medium for the growth of various microbes, which in turn contribute to the release and oxidation of new PUFA molecules. Due to dominance of linoleic acid (LA) among PUFAs, its oxidation of is the most important in meats. This study is the first attempt to quantitatively describe the oxidation of LA from start to finish, specifically to the toxic secondary oxidation product malondialdehyde (MDA). Oxidation begins after the release of LA from cell membrane phosphatidylcholines (PL), during which lysophosphatidylcholines (LPC) are formed under the catalysis of lipolytic phospholipases A (PLA 1 and 2) (EC 3.1.14). Process continues with combined sequential enzymatic and free-radical formation primary oxidation products called oxylipins (OL), and ends with the formation of secondary oxidation products, mostly various aldehydes, including MDA, which is toxic and mutagenic especially for bacteria. The two main enzymatic routes involved in LA oxidation are lipoxygenase (LOX) and cytochrome P450 oxidase (CYP450) pathways. Experimental. The lipolytic and oxidative processes in minced porcine, bovine, rainbow trout, and chicken meats were modified by six natural additives (powders of apple, black currant, aronia, tomato, garlic, and garden rhubarb (all 2% w/w)). During the 14-day storage at refrigerator temperature, the concentrations of LPCs 1 and 2 and MDA were determined periodically by LC-Q-ToF-MS and HPLC-DAD, respectively. Total counts of aerobic microorganisms and *Pseudomonas* spp. were estimated using ISO methods. Results. There is no clear correlation between concentration of MDA (or OLs) and LPC, but a zigzag temporal pattern exists that generally reflects the two main (lag- and log-) phases of the growth of aerobic microorganisms and *Pseudomonas* spp. During the first 1–4(6) days, the content of LPCs and MDA is positively correlated due to the autooxidation of LA. Mostly between days 6–8, the LPC content drops, whereas the production of OLs and MDA continues. The reserve of LPCs from autooxidation is obviously depleted around the 8th day. However, here the log phase of microbial growth starts, providing a fresh supply of LA and other PUFAs. The rapid increase in the content of LPCs and MDA after the 8th day is especially distinct in meat with tomato powder. Plant additives modulate the process by either accelerating or slowing down different phases. The described pattern is best visible in porcine meat, less so in beef and not at all in trout and chicken meats due to the low level of free LA throughout the whole oxidation process. Conclusion: In order to purposefully extend the shelf life of minced meats, in addition to the antibacterial and antioxidant (mostly radical scavenging) effects, the antilipolytic effects of additives should also be taken into account. The research in this topic is ongoing.

Keywords: lipolysis, phospholipase A, lysophosphatidylcholines, bacteria, PUFA oxidation.

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