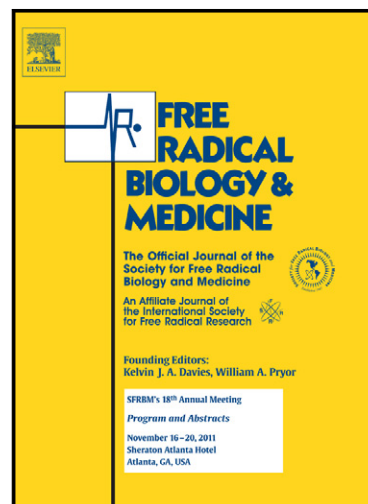


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Generation and esterification of electrophilic fatty acid nitroalkenes in triacylglycerides

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ABSTRACT

Electrophilic fatty acid nitroalkenes (NO₂-FA) are products of nitric oxide and nitrite-mediated unsaturated fatty acid nitration. These electrophilic products induce pleiotropic signaling actions that modulate metabolic and inflammatory responses in cell and animal models. The metabolism of NO₂-FA includes reduction of the vinyl nitro moiety by prostaglandin reductase-1, mitochondrial β-oxidation and Michael addition with low molecular weight nucleophilic amino acids. Complex lipid reactions of fatty acid nitroalkenes are not well defined. Herein we report the detection and characterization of NO₂-FA-containing triacylglycerides (NO₂-FA-TAG) via mass spectrometry-based methods. In this regard, unsaturated fatty acids of dietary triacylglycerides are targets for nitration reactions during gastric acidification, where NO₂-FA-TAG can be detected in rat plasma after oral administration of nitro-oleic acid (NO₂-OA). Furthermore, the characterization and profiling of these species, including the generation of beta oxidation and dehydrogenation products, could be detected in NO₂-OA supplemented adipocytes. These data revealed that NO₂-FA-TAG, formed by either the direct nitration of esterified unsaturated fatty acids or the incorporation of nitrated free fatty acids into

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