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Characterization of model triacylglycerol (triolein, trilinolein and trilinolenin) autoxidation products via high-performance liquid chromatography coupled with atmospheric pressure chemical ionization mass spectrometry

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Abstract

Oxidation products from the autoxidation of three triacylglycerol standards have been analyzed using reversed-phase high-performance liquid chromatography (RP-HPLC) coupled to mass spectrometry via an atmospheric pressure chemical ionization (APCI) source. Triolein, trilinolein and trilinolenin were autoxidized in the dark at 50–60°C until the oxidation products represented approximately 30% of the starting material. These oxidation product mixtures were then analyzed using RP-HPLC–APCI-MS. Several classes of oxidation products were directly detected and identified. Monohydroperoxides were present in the largest amounts in the oxidation products mixtures. The hydroperoxides were found to provide several structurally useful fragments: epoxide intermediates were formed which then underwent further fragmentation, and other fragments were formed from concerted loss of the hydroperoxide group to form a site of unsaturation. Fragments formed by intra-annular cleavage of epoxide intermediates allowed identification of several hydroperoxide isomers. Bishydroperoxides were observed which underwent similar fragmentation pathways. Mono- and diepoxides were also formed by the autoxidation reaction. Two classes of epoxides were observed: those in which an epoxide formed in place of an existing double bond, and those in which an epoxide formed away from a double bond. Two distinct fragmentation mechanisms were observed for epoxides which were not formed across a double bond. Other oxidation products which were observed included hydroxy trilinolenin, epidioxy trilinolenin and hydroperoxy, epidioxy trilinolenin.

Keywords: Fatty acids; Triacylglycerol oxidation products; Triolein; Trilinolein; Trilinolenin

1. Introduction

Autoxidation is a chemical reaction by which oxygen is added via a free radical mechanism to unsaturated fatty acids in vegetable oils like corn, canola and soybean oils. The initial compounds produced by autoxidation are hydroperoxides and hydroperoxide cyclic peroxides. The mechanisms of the reactions and the implications of the autoxidation reactions with vegetable oil unsaturated fatty acids have been thoroughly reviewed by Frankel [1], Porter et al. [2] and Hamilton et al. [3]. While the

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