Formation of Hydroperoxides in Steryl Fatty Acid Ester

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Phytosterols are added to various food products because of their known ability to lower serum cholesterol levels. Enriching may be accomplished by either free or esterified sterols. Under normal food processing conditions these compounds are rather stable, but oxidation products may be formed already during the manufacture of the sterol preparations leading to higher oxide contents in the final food products. Since some of the formed oxidation products may have negative health effects, it is essential to study the oxidation process of sterols, especially the initial state of the reaction. In this study, the effects of esterification on hydroperoxide formation of sterol were examined. Also the influences of fatty acid unsaturation level were compared. Cholesteryl stearate, oleate and linoleate, and free cholesterol were used as model compounds. Stock samples (i.e. without matrix) were maintained at 100 °C for 0–3 days and the formation of hydroperoxides (OOH's), both in the sterol and fatty acid parts, was followed in intact molecules by normal phase high performance liquid chromatographic method with evaporative light scattering detector (ELSD). Separation of the steryl ester hydroperoxides was performed on an alumina column by isocratic elution with 0.57% isopropanol in heptane (v/v). Free sterol hydroperoxides were determined with a silica column using gradient elution of 2–5% isopropanol in heptane (v/v) and diode array detector at 206 nm. Hydroperoxides in the sterol structure consisted mainly of 7α- and 7β-epimers. In unsaturated esters fatty acid 8-, 9-, 10- and 11-OOH, and 9- and 13-OOH were formed. Though sterol part hydroperoxides were formed rapidly in cholesteryl linoleate, the measurable amount of sterol part OOH's reached only 10 mg/g indicating possible further reactions into secondary oxidation products. Whereas in cholesteryl oleate the amount of OOH's reached 50 mg/g and in cholesteryl stearate even 100 mg/g indicating OOH's to be more stable in these compounds. In free cholesterol only 2.6 mg/g of OOH's were determined after three days. In conclusion, esterification seemed to expose sterol for oxidation at 100 ºC and unsaturation level of the fatty acid affected the measurable amount of formed hydroperoxides.