Structural and External Factors Affecting the Oxidation of Sterols. M. Lehtonen, A.M. Lampi, and V. Piironen, University of Helsinki, Helsinki, Finland.

Plant sterols and their conjugates are both naturally present in foods and they may be added into novel food products. Since the oxidation products of sterols may have harmful biological effects, their formation should be prevented during food processing and storage. This study investigated the effects of chemical (i.e., esterification, unsaturation degree of the acyl moiety and sterol structure) and external (i.e., temperature and medium) factors on the oxidation of sterols. The introduction of an acyl moiety to a sterol altered the physical state and polarity of the sterol and thus affected its oxidation. The increased unsaturation of the acyl moiety increased the oxidation rate of both the steryl and acyl moieties. No differences in the initial reactivities of these two moieties were observed, but they oxidised concomitantly. Both the increased temperature (100<140<180°C) and the increased unsaturation of the lipid medium intensified the oxidation of steryl esters and free sterol. The formed steryl ester and free sterol hydroperoxides decomposed into traditionally determined sterol secondary oxidation products and also underwent polymerisation as a rival reaction. In conclusion, by altering the chemical and physical properties of sterols, their deterioration reactions can be altered.

The Degree of Lipophilization Affects Antioxidative Efficacy of Ferulates in Omega-3 Enriched Milk.

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Foods containing omega-3 PUFA are highly susceptible to oxidation. One strategy to limit lipid oxidation is addition of antioxidants. The efficacy of antioxidants can vary with the complexity of the food matrix. Lately, extensive work has been performed on phenolipids and their antioxidant efficacy in model emulsion systems. Results indicated a cut-off effect in relation to the alkyl chain length grafted to the phenolic compounds. The impact of emulsion composition on the antioxidant activity has previously been

demonstrated for caffeates in milk and mayonnaise. Different critical chain lengths (cut-off) were observed for the two food systems. Thus, a better understanding of the antioxidative effect of phenolipids in complex foods is of great interest. The aim of this study was to evaluate the antioxidative effect of ferulic acid and its esters, ferulates, in fish-oil-enriched milk. Lipid oxidation was evaluated from 3 parameters measured over storage time: peroxide value, volatiles and tocopherol concentrations. The results demonstrated that the composition of food emulsions influenced the antioxidative effect of ferulates. Depending on the lipophilization degree, ferulates acted surprisingly either as antioxidants or prooxidants. These results were more complex than what was expected from the cut-off hypothesis.

Synthesis and Antiradical Properties of Novel Diacylglycerols Rosmarinate Conjugates. P. Villeneuve, C. Bayrasy, E. Durand, and J. Lecomte, UMR IATE CIRAD, Montpellier, France.

In compartmentalized systems, it is generally considered advantageous for antioxidants to exhibit surface activity. Surface-activity, hence hydrophobicity, allows the antioxidant to fuse with lipid-water interfaces and membranes and to be efficiently taken up by living cells. Thus, hydrophobic antioxidants are supposedly more internalized within cells than their hydrophilic counterparts. As such, they are thought to more effectively deal with the many reactive oxygen species (ROS) released into the cytosol. One reliable strategy to design a surface-active antioxidant is to incorporate positioned lipophilic groups by lipophilization. To date, a multitude of lipophilized antioxidants have been synthesized to obtain multifunctional compounds called "phenolipids". To have a global picture of the role of the lipophilic moiety on antioxidant activity, we tested other lipophilic moieties consisting of diacylglycerols grafted onto rosmarinic acid. Accordingly, herein is described a chemo-enzymatic route to prepare these 1,2diacylglycerol rosmarinate conjugates with various chain lengths These phenolipids so prepared were then finally assessed for their antioxidant activity in a ROS-overexpressing cell line of human dermal fibroblasts.