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Synthesis of steryl ferulates with various sterol structures and comparison of their antioxidant activity

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ABSTRACT

Steryl ferulates synthesised from commercial sterols as well as commercial oryzanol were used to better understand how structural features affect antioxidant activity *in vitro* by the ABTS$^{\cdot+}$ radical decolorization assay, by oxidative stability index (OSI) of soybean oil, and by analysis of antioxidant activity during frying. Steryl ferulates inhibited the ABTS$^{\cdot+}$ radical by 6.5–56.6%, depending on their concentration, but were less effective, especially at lower concentrations, than ferulic acid. Ferulic acid and steryl ferulates had either no effect, or lowered the OSI of soybean oil by up to 25%, depending on the concentration. In their evaluation as frying oil antioxidants, steryl ferulates with a saturated sterol group had the best antioxidant activity, followed by sterols with one double bond in the C5 position. The results indicate that a dimethyl group at C4 as well as a C9,C19 cyclopropane group, as found in oryzanol, negatively affects antioxidant activity in frying oils.

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1. Introduction

Steryl ferulates are composed of ferulic acid esterified to plant sterols and found in the inner pericarp and aleurone layer of cereals grains such as corn, wheat, rice, rye, and triticale (Moreau, Singh, Nuñez, & Hicks, 2000; Norton, 1995; Seitz, 1989). Steryl ferulates from rice bran oil, which are called γ-oryzanol (oryzanol for short), are mainly composed of two 4,4′-dimethylsterols, cycloartenol and 24-methylene-cycloartanol, as well as the 4-desmethylsterol, campesterol, and low amounts of other 4-desmethyl sterols (Xu & Godber, 1999). Corn steryl ferulates consist mainly of two saturated 4-desmethylsterols, sitostanol, and campestanol, with lower amounts of other 4-desmethylsterols such as sitosterol and campesterol (Seitz, 1989).

Ferulic acid is a well-known phenolic antioxidant, thus steryl ferulates have antioxidant activity due to the radical scavenging activity of the phenolic component (Juliano, Cossu, Alamanni, & Piu, 2005; Kikuzaki, Hisamoto, Hirose, Akiyama, & Taniguchi, 2002; Nyström, Achrenius, Lampi, Moreau, & Piironen, 2007; Nyström, Mäkinen, Lampi, & Piironen, 2005; Suh, Yoo, & Lee, 2007; Xu & Godber, 2001). The hydrophobic sterol group allows steryl ferulates to be soluble in oils, making them excellent candidates for antioxidants in oil-rich foods. In addition, because of the increased molecular weight of steryl ferulates compared to ferulic acid, steryl ferulates are less likely to evaporate at high temperatures such as in frying oils and in other high temperature food processes. Steryl ferulates are also less susceptible to thermal decomposition as compared to non-esterified ferulic acid (Shopova & Milkova, 2000). Nyström et al. (2007) demonstrated that 0.5% and 1.0% sitostanyl ferulate inhibited polymer formation in stripped high oleic sunflower oil (HOSUN) heated to 180 °C by 27% and 43%, respectively. In previous frying studies, we found that corn steryl ferulates inhibited polymerisation of soybean oil by up to 70%, whereas oryzanol was much less effective (Winkler-Moser, Rennick, Palmquist, Berhow, & Vaughn, 2012). Corn steryl ferulates also protected the endogenous tocopherols in soybean oil during frying, whereas oryzanol did not. It was also noted that oryzanol degraded at a faster rate during frying compared to corn steryl ferulates. It was hypothesised that higher stability was the reason for the better anti-polymerisation activity; however, in a heating study (180 °C, in soybean oil), corn steryl ferulates actually degraded at a faster rate compared to oryzanol, but still had better antipolymerisation activity (Winkler-Moser, Rennick, Hwang, Berhow, & Vaughn, 2013), indicating that the differences in activity may not be completely attributed to their stability. In fact, Nyström et al. (2005) observed stronger antioxidant activity for wheat and

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rye steryl ferulates compared to oryzanol and cycloartenyl ferulate in methyl linoleate oxidised at 40 °C, which is not likely to be related to thermal stability.

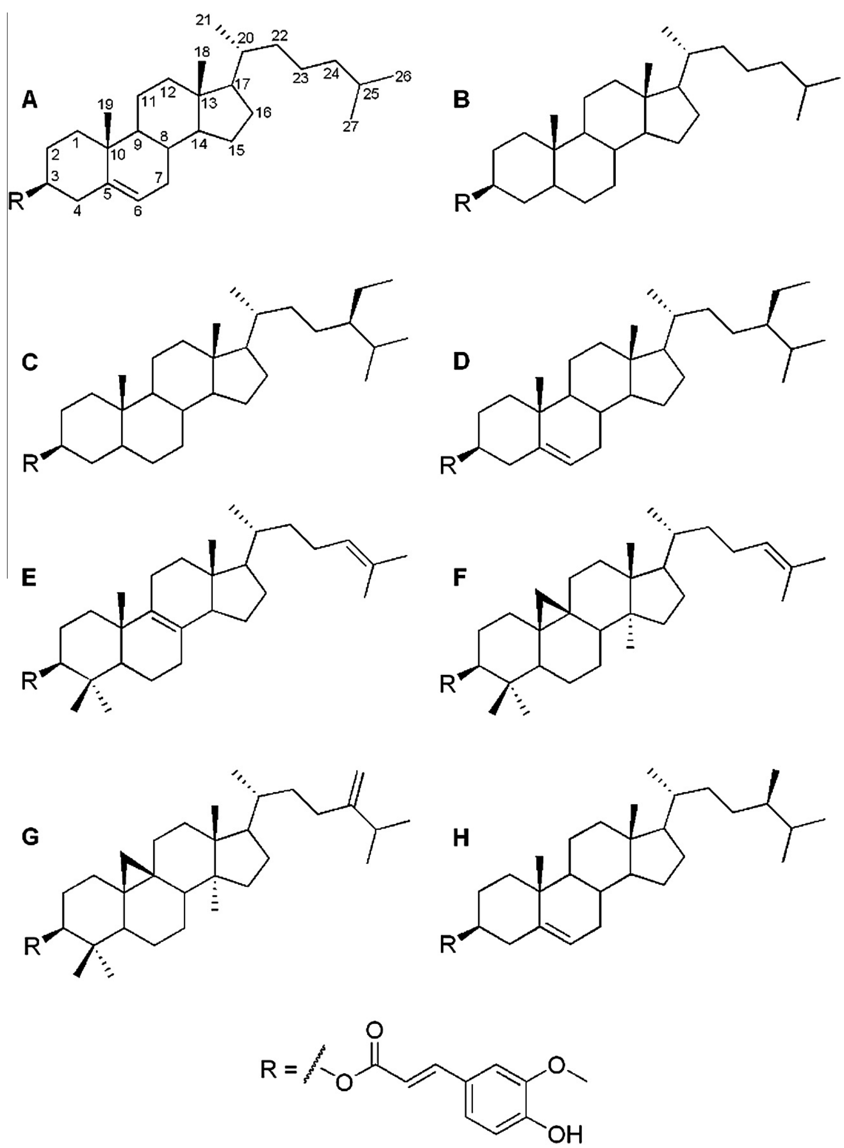
Since the only difference between oryzanol and corn steryl ferulates are in the structures of the phytosterol moieties, the objective of this research was to conduct studies to further understand the effect of structural features of the phytosterol head group on antioxidant activity. Since isolation and purification of the quantities needed to carry out these analyses would require large amounts of starting material, as well as solvents, we chose to synthesise steryl ferulates using pure phytosterols. Previously published synthesis techniques (Condo, Baker, Moreau, & Hicks, 2001; Ebenezer, 1991) were improved for time, solvent consumption, and yield, and the antioxidant activity of synthetic steryl ferulates as well as oryzanol and ferulic acid were evaluated *in vitro* and by analysis of oxidative stability index in soybean oil, as well as in frying studies in soybean oil.

The structures of the steryl ferulates that were synthesised are shown in Scheme 1. Cholesterol (A) and sitosterol (D) were chosen to represent sterols with a double bond at the C5-position, which should provide information about the effect of this double bond on steryl ferulate activity. Sitosterol, stigmasterol, campesterol, and brassicasterol are the four most common plant sterols, and they all have a C5 double bond. Since the majority of corn steryl ferulates have saturated (no double bonds) phytosterols, β-cholestanol (B) and sitostanol (C, also called stigmastanol) were chosen as model compounds for this group. Finally, lanosterol (E) was chosen to study the effect of the dimethyl group at C4, which is a structural feature that is also found in the two major steryl ferulates found in oryzanol, cycloartenol (F) and 24-methylene cycloartanol (G). These two sterols were not commercially available in the quantities needed for this study, so commercially available oryzanol was studied instead. Also shown in Scheme 1 is campesterol (H), which together with sitosterol makes up a low percentage of corn steryl ferulates (∼14%), but makes up about 31% of oryzanol.

2. Materials and methods

2.1. Materials

8,24,(5-α)-Cholestadien-4,4,14-α-trimethyl-3-β-ol (lanosterol, ∼65%) was purchased from Steraloids Inc. (Newport, RI). ABTS



Scheme 1. Structures of synthetic steryl ferulates: (A) cholesterol, (B) cholestanol, (C) sitostanol, (D) sitosterol, (E) lanosterol, and structures of steryl ferulates in oryzanol: (F) cycloartenol, (G) 24-methylene cycloartanol, (H) campesterol. R = *trans*-ferulic acid.