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Phenylpropanoid esters of lesquerella and castor oil☆

David L. Compton*, Joseph A. Laszlo, Kervin O. Evans

Renewable Product Technology Research Unit, United States Department of Agriculture, Agricultural Research Service, National Center for Agricultural Utilization Research, 1815 N. University Street, Peoria, IL 61604, USA

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ABSTRACT

Lesquerella (LO) and castor oil (CO) were esterified at the secondary hydroxyl groups of their 14-hydroxyeicos-*cis*-11-enoic fatty acids and 12-hydroxyoctadec-*cis*-9-enoic fatty acids, respectively, with 4-acetoxy-3-methoxycinnamic acid (acetoxyferulic acid). The unconventional esterifications were conducted under inert nitrogen atmospheres without solvent at 175–200 °C in sealed ampules. ^{1}H NMR was used to measure the degree of acetoxyferuloyl esterification using a modified esterification number (EN). Reactions at 200 °C resulted in ~43% conversions to the acetoxyferuloylated LO and CO but promoted significant degradation/loss of the acetoxyferulic acid as evidenced by the low quantity of acetoxyferulic acid found in the reaction products as determined by HPLC. Reactions at 175 °C resulted in significantly lower conversions to the acetoxyferuloylated LO and CO, 9–17%, but did not result in as severe acetoxyferulic acid degradation. The addition of tin (II) 2-ethylhexanoate catalyst to the 175 °C reactions increased esterification conversion to ~45% without significant loss of acetoxyferulic acid to degradation. The aromatic acetate of the acetoxyferuloylated LO and CO was selectively deacylated using excess pyrrolidine without affecting the aliphatic esters to give feruloylated LO and CO. The feruloylated LO and CO absorbed ultraviolet (UV) radiation from 280 to 360 nm with a λ_{max} at 327 nm, bridging the absorbance gap of commercial UV absorbing ingredients. The feruloylated LO and CO are also presumably good antioxidants and are potential candidates for incorporation into lipid bilayers to protect liposomes and their contents from reactive oxygen species.

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1. Introduction

The functionalization of triacylglycerols (TAG) with phenolic plant components has resulted in compounds that have garnered much interest from the cosmetic and skin care industry (Compton and Laszlo, 2002; Compton et al., 2006; DeFilippi et al., 2010). Phenylpropanoids (*e.g.* caffeic acid, coumaric acid, ferulic acid, sinapic acid) are natural plant components that possess excellent antioxidative properties as well as ultraviolet (UV) absorbing capabilities (Cooper et al., 1978; Graca and Pereira, 2000; Rozema et al., 2001; Ruhland and Day, 2000). The cosmeceutical industry has long desired to incorporate these phenylpropanoids into cosmetic and skin care formulations; however, these isolated phenolic compounds possess poor lipophilic solubility, significant water solubility (with a propensity to wash off the skin), and yellow on the skin when exposed to UV radiation.

The transesterification of phenylpropanoids to the glycerol backbone of TAG has alleviated the formulation problems of the natural phenolic acids. An early example of this chemistry is the preparation of mono-, di-, and tricaffeoyl TAGs by the esterification of the mono-palmitoylglycerol with caffeic acid chloride in the presence of anhydrous chloroform (King, 1964). The process involves the chemical protection of the phenyl hydroxyl groups followed by their subsequent deprotection after esterification to the glycerols. These compounds were tested for their antioxidant activity in foodstuffs, animal feed, and vegetable oils. More recently the transesterification of vegetable oils with ferulic acid has been accomplished enzymatically without the need for chemical catalysts or organic solvents. Soybean oil can be transesterified with ferulic acid ethyl ester using Novozym 435 (immobilized *Candida antartica* lipase B) (Laszlo et al., 2003). The resultant feruloylated lipids possess excellent organic solubility, allow penetration of the phenolic moieties into the epidermis, have low water solubility, and do not yellow when applied to the skin, while retaining the essence of an all natural ingredient (DeFilippi et al., 2010).

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* Corresponding author. Tel.: +1 309 681 6321; fax: +1 309 681 6040.
E-mail address: david.compton@ars.usda.gov (D.L. Compton).

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The esterification of hydroxyl oils with phenylpropanoids is another method for incorporating the phenolic functionality into TAG. Hydroxy oils (*e.g.* castor oil) and their free hydroxyl fatty acids are used in cosmetic and skin care formulations as humectants to moisturize the skin and also act as mild exfoliants. The hydroxyl oils and waxes are cosmeceutically desirable because of their non-comedogenicity (tendency to create "blackheads" or other skin blemishes) and good emolliency. The olefin bonds in jojoba wax have been epoxidized and ring-opened to form tertrahydroxyjojoba wax which was then esterified with 4-methoxycinnamic acid using conventional base catalysis (Touitou and Bergelson, 2002). 4-Methoxycinnamic acid is a non-natural, petroleum-based compound and its ethylhexyl ester is used ubiquitously in sunscreen formulations as a FDA-approved sunscreen active ingredient (Shaath, 1997). Attempts to esterify ferulic acid (4-hydroxy-3-methoxycinnamic acid), a natural alternative to 4-methoxycinnamic acid, to hydroxy-modified jojoba wax and milkweed oil has been reported (Harry-O'kuru, 2005; Harry-O'kuru et al., 2005).

We previously reported that lesquerella oil (LO) and castor oil (CO) can be esterified with cinnamic and 4-methoxycinnamic acids at high temperatures with and without the use of a chemical catalyst (Compton et al., 2004). *Physaria* (formerly *Lesquerella) fendleri* is being developed as an alternative crop in the southwestern U.S. The seed oil contains 55–60% of 14-hydroxyeicos-*cis*-11-enoic acid (C20:Δ11, 14-OH) and is a potential domestic alternative to ricinoleic acid, 12-hydroxyoctadec-*cis*-9-enoic acid (C18:Δ9,12-OH), obtained from castor oil (CO) (Cermak et al., 2006). The work herein details the esterification of the hydroxyl fatty acids of LO and CO with 4-acetoxy-3-methoxycinnamic acid followed by the deprotection of the ferulic acid hydroxyl group to afford feruloylated LO and CO. Ferulic acid is a preferable phenolic moiety compared to 4-methoxycinnamic acid for use in cosmeceuticals because it is a natural compound with inherent antioxidation properties to quell inflammatory tissue processes. Also, LO and CO naturally contain hydroxyl fatty acids and are a preferable natural feedstock compared to the hydroxyl-derivatized jojoba and milkweed oils described above.

We have shown that the antioxidant capacity of vegetable oils transesterified with ferulic acid on the glycerol moiety (*i.e.* feruloyl di-γ-linolenoylglycerol) prevents the oxidation of polyunsaturated fatty acid oils in model membrane phospholipid vesicles (Laszlo et al., 2012b). Of interest is the co-location of the feruloyl moiety in relation to the phosphotidylcholine head groups of the model lipid bilayers (Laszlo et al., 2010). The feruloylated LO and CO molecules described herein have the feruloyl moiety distally attached to the TAG relative to the glycerol moiety and can be used comparatively to feruloyl di-γ-linolenoylglycerol to determine if the proximity of the feruloyl group to the glycerol moiety influences the position (depth) of the feruloyl group in the phospholipid bilayers or its antioxidant efficacy. The feruloylated LO and CO are preferable to the hyper-feruloylated jojoba or milkweed oils described above because the feruloylated LO and CO retained some desaturation and lipophilicity and should better incorporate into the lipid bilayers.

2. Experimental

2.1. Materials

Lesquerella oil (LO, Fig. 1), with an average molecular mass of 975 g/mol (Isbell and Cermak, 2002) was obtained from cold-pressed *Physaria fendleri* seed. The oil was alkali refined, charcoal bleached and deodorized. Acetic anhydride, ammonium chloride castor oil (CO), 4-hydroxy-3-methoxycinnamic acid (ferulic acid), 4-hydroxy-3-methoxycinnamic acid (ethyl ferulate), tin (II) 2-ethylhexanoate, pyrrolidine, magnesium sulfate, sulfuric acid and thionyl chloride were purchased from Sigma–Aldrich (St. Louis, MO) and used as obtained. Escalol 557 (octinoxate), Escalol 507 (padimate-O), Escalol 517 (avobenzone), and Escalol 567 (oxybenzone) were generously donated by ISP Technologies, Inc. (Assonet, MA). Anhydrous pyridine (<0.005% water), THF (<0.005% water), and toluene (<0.005% water) were obtained from Sigma–Aldrich in Sure/Seal® bottles. All other solvents were reagent grade and used as obtained.

2.2. Synthesis of 4-acetoxy-3-methoxycinnamic acid (**1**)

The reaction was adapted from that of Hatfield et al. (1991), performed under a nitrogen atmosphere, using standard Schlenk line techniques. Ferulic acid (20 g, 0.103 mol) was dissolved in 35 ml of anhydrous pyridine at room temperature. Excess acetic anhydride (32 ml, 0.304 mol) was added to the pale yellow solution slowly *via* syringe, and the solution stirred for 4 h. The reaction was quenched with 100 ml of 95% ethanol and cooled at 10 °C for 1 h. The resultant white solid was collected by filtration. The filtrate was reduced to a white solid under vacuum at 80 °C. The solid was dissolved in 25 ml of warm toluene, 25 ml of 95% ethanol was added, and the suspension cooled at 10 °C for 1 h. The second crop of crystals was collected by filtration. The crops of white solid were combined, washed with 3 × 50 ml portions of 95% ethanol, and dried *in vacuo* at 80 °C for 24 h. Yield: 19.15 g (78.7%), mp 198–200 °C, ^{1}H NMR (500 MHz, d_6-acetone) δ 12.40 (*s*, 1 H, -C(O)-O*H*), 7.62 (*d*, 1 H, H-7), 7.43 (1 H, d, H-2), 7.22 (*dd*, 1 H, H-6), 7.08 (*d*,1 H, H-5), 6.51 (*d*, 1 H, H-8), 3.87 (*s*, 3 H, -O-CH_3), 2.22 ppm (*s*, 3 H, -O-C(O)-CH_3)

2.3. Synthesis of 4-acetoxy-3-methoxycinnamic acid chloride (**2**)

The reaction was adapted from that of Hatfield and coworkers (Hatfield et al., 1991), performed under a nitrogen atmosphere, using standard Schlenk line techniques. **1** (16.96 g, 0.072 mol) was slurried in 200 ml of anhydrous toluene at room temperature. Thionyl chloride (21.0 ml) was added dropwise by syringe. The slurry was heated at 95 °C with stirring for 5 h (**1** dissolved within 10 min). The clear yellow solution was allowed to cool, and the toluene was removed under vacuum at 70 °C. The resultant solid was allowed to cool to room temperature and was dissolved in 200 ml of chloroform. The solution was filtered through a bed of celite, and the celite was washed with 2 × 25 ml portions of chloroform. The filtrate and washings were combined, and the chloroform was removed *in vacuo* at 50 °C. The resultant off-white solid was dried at 70 °C *in vacuo* for 24 h. Yield: 16.02 g (87.6%), mp 131–135 °C, ^{1}H NMR (500 MHz, d_6-acetone) δ 7.91 (*d*,1 H, H-7), 7.59 (*d*,1 H, H-2), 7.40 (*dd*, 1 H, H-6), 7.15 (*d*, 1 H, H-5), 6.90 (*d*, 1 H, H-8), 3.89 (s, 3 H, -O-CH_3), 2.24 ppm (*s*, 3 H, -C(O)-CH_3).

2.4. Synthesis of 4-acetoxy-3-methoxycinnamoyl lesquerella (**3**) and castor (**4**) oils

The procedure was modified from that of Touitou and Bergelson (2002) and was conducted under nitrogen using standard Schlenk line techniques. A typical reaction consisted of dissolving **2** (1.66 g, 6.52 mmol) in 30 ml of anhydrous chloroform. A solution of lesquerella oil (3.18 ml, 3.10 mmol) and excess pyridine (5.0 ml, 61.8 mmol) in 30 ml of chloroform was placed in an addition funnel and added dropwise to the **2** solution with stirring over 45 min. After the addition was complete the bright yellow solution was heated to 50 °C for 24 h. The resultant light, pale yellow solution was allowed to cool and was washed in air sequentially with 50 ml portions of water, 10% aqueous sodium hydroxide, and water. The chloroform layer was dried over anhydrous magnesium sulfate, filtered, and the solvent removed *in vacuo* at 40 °C. The residue

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