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Synthesis and characterization of tetrahydroxyjojoba wax and ferulates of jojoba oil

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Abstract

The new crop oil from jojoba (*Simmondsia chinensis*) is a skin-softener similar to sperm whale oil. In an effort to find new uses of this oil, we have converted jojoba liquid wax into two new products in mild chemical processes. Tetrahydroxyjojoba wax (THJF) is a colorless, stable, low-melting solid and jojoba ferulate, an ultra violet (UV) absorbing species by esterification of the tetrahydroxy wax with *trans*-4-hydroxy-3-methoxycinnamic acid. The tetrahydroxyjojoba wax like the parent oil has no UV radiation absorbing property, but it is an excellent emollient. In contrast, the jojoba ferulate is a good UV absorber. Differential scanning calorimetry of the ferulate, its precursor, the tetrahydroxyjojoba wax, and the acetylated jojobaferulate derivatives indicate very stable properties from ambient to 100 °C temperature range.
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Keywords: Diepoxyjojoba wax; Hydroxyjojoba wax; Vegetable oils; New crop oils; Liquid wax ferulates; UV-absorption

1. Introduction

Jojoba (*Simmondsia chinensis*) is a semi-arid shrub native to Arizona, California and northern Mexico. The seed contains 50–60% oil. The oil is a unique liquid wax ester comprising mainly C40:2 and C42:2 and is regarded as a replacement for sperm whale oil. Jojoba oil also contains C38:2, C44:2, and C46:2 components formed from C18:1, C20:1, C22:1, and C24:1 carboxylic acids and alcohols (Miwa, 1971). The structure of jojoba oil is such that it acts as a natural skin-softener. Consequently, jojoba oil is incorporated into many personal care formulations. Jojoba oil is marketed extensively in the cosmetic and lubricant industry, where 70% of the US production is exported. Some chemical modification of the oil has

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occurred and has been geared toward polyunsaturated derivatives via bromination followed by dehydrohalogenation to produce alkynes and tetraene intermediates. These polyunsaturates were used for Diels–Alder type reactions with suitable dienophiles (Binman et al., 1996a,b, and 1998; Shevachman et al., 2001). Zabicky and Mhasalkar (1986) also modified jojoba oil through preparation of diozonides of the oil, which were then converted to the corresponding aldehydes and dicarboxylic acids. Recently, in the search for new value-added uses of traditional vegetable oils, Compton et al. (2000) and Compton and Laszlo (2001) have enzymatically transesterified soybean oil with ethyl ferulate to give the feruloylglycerols having UV absorbing characteristics.

Although some components of native jojoba seed meal, simmondsin, has ferulate analogs that absorb UV radiation, jojoba oil has no UV absorbing properties. In an effort to explore new uses and new markets for jojoba oil, we have developed the tetrahydroxy wax and a novel UV absorbing species by incorporation of several molecules of *trans*-4-hydroxy-3-methoxycinnamic acid (ferulic acid) into the structure of the tetrahydroxyjojoba wax (THJF) or to the diepoxyjojoba wax (EPF).

2. Materials and methods

2.1. Materials

Ferulic acid (99%), ethyl acetate, hydrochloric acid, and formic acid (96%) were from Fisher Scientific, (Chicago, IL). Hydrogen peroxide (50% in water) and anhydrous $ZnCl_2$ were from Aldrich Chemical Company, (St. Louis, MO). Jojoba oil was extracted from jojoba seed stock from Purcell Jojoba International, Avila Beach, CA.

2.2. Instrumentation

Differential scanning calorimetric thermograms were recorded using a modulated differential scanning calorimeter, 2920 MDSC, (TA Instrument, New Castle, DE). Melting points were also measured either on a Mel-Temp II, (Scientific Devices, Holliston, MA) equipped with digital readout or on a Fisher–Johns melting point apparatus and the melting point values were uncorrected. Fourier transform infrared (FTIR) spectra were determined on a Bomem MB-Series, spectrometer, (Quebec, PC, Canada). ^{1}H and ^{13}C NMR spectra were generated on a Bruker ARX-400 with a 5 mm dual proton/carbon probe (Bruker Spectrospin, Balerica, MA), using tetramethyl silane or $CHCl_3$ as the internal standard. Field desorption mass spectra (FD-MS) and fast atom bombardment mass spectra (FAB-MS) were obtained from the University of Illinois, Champaign-Urbana Mass Spectrometry Service Center. Thin layer chromatography (TLC) was performed on precoated silica gel plates K6F, 60 A (Whatman; Maidstone, England) developed as indicated and visualized by spraying with methanol:H_2SO_4 (3:1) and heated to 110 °C. The ferulate derivatives did not require spraying as these were visible under the UV lamp. UV spectra of relevant compounds were recorded on a Shimadzu UV–vis mini 1240 spectrophotometer (Kyoto, Japan).

2.3. Methods

DSC measurements samples (7–10 mg ± 0.1 mg) were hermetically double-sealed in coated aluminum pans. Conditions were set at 3 °C/min from ambient to 100 °C and cooled to −25 °C for both samples including 0.2 W/s sensitivity. The samples were cycled between 100 and −25 °C five times with modulation ±1.00 °C every 80 s. The DSC was calibrated against an indium standard. During each run, the N_2 flow rate was 24 cm^3/min. Calculations were made based on the corrected sample weight.

2.3.1. Synthesis of diepoxyjojoba wax

Jojoba oil (201.0 g, 326 mmol) was placed in a 1.0 L jacketed round-bottomed flask (RBF) equipped with a mechanical stirrer and heated to 40 °C. Formic acid (12.5 g, 272 mmol) was added in one portion and the mixture stirred to homogeneity. Hydrogen peroxide (69.5 g, 2.042 mol) was then added slowly. After the completion of hydrogen peroxide addition, the temperature was raised to 70 °C and reaction monitored by thin layer chromatography on silica gel with hexanes/ethyl acetate (1:1) as eluting solvent system. The TLC plates were visualized by spraying with methanol:H_2SO_4 (3:1) and heated to 110 °C. The reaction was complete in 3 h. The heat source was then removed, stirring was stopped, and reaction mixture was allowed to cool to

room temperature. The white spherical crystals formed were filtered and rinsed with ethyl acetate and dried. The ethyl acetate wash was added to the bulk of the reaction mixture, which was then diluted with more ethyl acetate (300 ml) and transferred to a separatory funnel. The mixture was washed with saturated Na_2CO_3 solution (100 ml × 3) followed with saturated NaCl solution. The organic phase was then dried (Na_2SO_4) and concentrated to give an over all yield of 205 g (96.7%). The melting point of the solid jojoba diepoxide was 58.4–59 °C. The FTIR (KBr) spectrum gave the following absorbances in cm^{-1}: 2954 m-s, 2918 very strong (vs), 2851 s, 1730 m, 1470 m, 1211 w, 1191 m, 848 m, 723 m; whereas the FTIR spectrum (KBr_{film}) cm^{-1} of the major fraction was: 2954 m-s, 2918 vs, 2850 s, 1732 m-s, 1465 m, 1206 w-m, 1181 m, 844 m, 721 m. The ^1H NMR ($CDCl_3$) gave δ: 4.06 t (J = 6.7 Hz, 2H), 2.91 m (4H), 2.30 t (J =7.4 Hz, 2H), 1.62 m (4H), 1.51–1.29 m (62H), 0.89 t (J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ: 174.05, 64.47, 57.31, 34.47, 31.93, 29.67, 29.62, 29.60, 29.43, 29.32, 29.29, 29.22, 28.73, 27.90, 26.68, 26.01, 25.08, 22.73, 14.16.

In comparison, the spectra of the unmodified jojoba oil show a FTIR (smear on KBr) cm^{-1}: 3004 m, 2954 sh, 2925 vs, 2854 s, 1739 s, 1655 w, 1463 m-s, 1353 m, 1247 m, 1172 m-s, 722 m; ^1H NMR ($CDCl_3$) δ: 5.35 t (J = 9.8 Hz, 4H), 4.06 t (J =13.5 Hz, 2H), 2.30 t (J =15.1 Hz, 2H), 2.02 m (8H), 1.62 m (4H), 1.28 bs (54H), 0.89 t (J = 13.7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ: 174.0, 129.97, 129.92, 129.89, 64.44, 34.46, 32.00, 29.85, 29.77, 29.73, 29.61, 29.57, 29.53, 29.41, 29.36, 29.25, 28.75, 27.28, 26.03, 25.10, 22.76, 14.17. The FD-MS^+ gave: m/z 560.5 (C38, 15%), 588.5 (C40, 78%), 616.5 (C42, 100%), 644.5 (C44, 24%), 672.5 (C46, 5%).

2.3.2. Synthesis of tetrahydroxy jojoba oil derivative

Jojoba oil (359 g, 582.2 mmol) and formic acid (22.5 g, 384.6 mmol) were placed in 1.0 l, jacketed RBF fitted with a mechanical stirrer and heated to 40 °C. The mixture was stirrred vigorously and H_2O_2 added slowly. At the completion of peroxide addition, the temperature was raised to 70 °C and the reaction progress monitored every 30 min by TLC as described earlier for the epoxide reaction and by FTIR for the diagnostic 844 cm^{-1} band. At the end of 4 h, the reaction was complete. The yellow color of the reaction mixture was discharged. Heating and stirring were discontinued to cool the colorless product mixture. When the temperature was below 30 °C, the separated aqueous phase was discarded and deionized water (250 ml) was added to the product followed with concentrated HCl (25.0 ml, approximately 1.1 M). The opaque mixture was placed in a 50 °C water bath and stirred. After 4 h, the disappearance of the 844–848 cm^{-1} bands indicated complete epoxide ring opening. The mixture was then cooled to room temperature, transferred to a separatory funnel with ethyl acetate (600 ml) and washed with saturated Na_2CO_3/NaCl solutions until about pH 7 was reached. The organic layer was then dried (Na_2SO_4) and concentrated in vacuo to yield 371 g (93%) crude tetrahydroxyjojoba wax ester, a solid with low melting point of 34–37 °C. Cyclic DSC thermograms of the sample showed a melting range of 19–31 °C. The FTIR (KBr_{film}) of the solid (cm^{-1}) was 3636–3116 (OH), 2951 (CH_3 asym), 2922 (CH_2 asym), 2851 (CH_3,CH_2 sym), 1737 (C=O), 1468 (–CH_2– deformation), 1377 (CH_3 deformation), 1241 (–O–C(O)–C– stretch), 1182 (–HC–C–OH), 1100 (–HC–OH–C), 1076 (HC–HC–OH–C), 902, 709. The ^1H NMR ($CDCl_3$) δ (ppm) was 4.05 t (J = 13.5 Hz, 2H), 3.89 m (2H), 3.60 m (2H), 2.28 t (J = 7.8 Hz, 4H), 1.79 q (J =7.8, 7.4 Hz, 4H), [1.63 q (J = 7.1, 7.1 Hz; 1.55 q (J = 14.3, 11.9 Hz; 1.42 q (J = 14.7, 13.4 Hz; 1.28 bs (64H)], 0.88 t (J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ: 174.07 (–C=O), 73.96 (–CHOH), 69.12 (–CHOH), 64.47 (–CH_2O–), 34.94 (–CH_2C=O), 34.68 (–CH_2CHOH–), 34.45 (–CHCHOH–), 31.93 (–CH_2CH_2CHOH–), 31.91 (–CH_2CH_2CHOH–), 29.76, 29.62, 29.58, 29.53, 29.49, 29.43, 29.40, 29.31, 29.29, 29.21, 28.71, 26.76, 25.99, 25.71, 25.06, 22.72 (–CH_3), 14.16 (–CH_3).

2.4. Ferulation of jojoba wax derivatives

2.4.1. Jojoba ferulate

Diepoxy jojoba wax ester (13.40 g, 20.66 mmol), ferulic acid (8.40 g, 43.26 mmol), dry toluene (200 mL) together with para-toluenesulfonic acid (TsOH, 0.40 g) were placed in a dry 500 ml, 2-necked reaction flask fitted with a mechanical stirrer. The contents of the flask were stirred; and a catalytic amount of concentrated HCl (3 drops) was added and the mixture heated to gentle reflux for 72 h. The reaction mixture was then cooled and transferred into a separatory funnel and

washed with saturated $NaHCO_3$ to pH 6.5. The organic phase was then dried (Na_2SO_4) and concentrated under reduced pressure. The residue was vacuum liquid chromatographed (VLC) in hexanes/ethyl acetate to give 12.0 g, (42.9%) of reddish semi-solid ferulates based on the tetraferulate. A solution of the purified compound in ethyl acetate gave a UV spectrum having two bands observed at 321.5 nm and at 254 nm wavelengths. The FTIR (KBr_{film}) cm^{-1} showed 3464 m, 2925 vs, 2854 s, 1737 s, 1633 w, 1603 w, 1519 w, 1467 m, 1373 m, 1240 s, 1173 m, 1072, 1026, 726. The ^1H NMR ($CDCl_3$) δ had 7.63 d (J = 15.9 Hz, 2H), 7.04 d (J = 2 Hz, 3H), 6.90 d (J = 8.1 Hz, 2H), 6.30 d (J = 15.9 Hz, 2H), 5.20 bs (OH, 2H), 4.10 q (J = 14.3 Hz, 2H), 4.02 bs (OH, 2H), 3.91 s (9H), 2.25 t (J = 23.8 Hz, 2H), 2.02 s (6H), [1.73 bs; 1.58 bs, 1.24 bs (71H)], 0.84 t (J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ: 174.0 (–CO_2-alkyl ester), 171.2 (–O–C=O conjugated ester), 166.7 (–CO_2 conjugated ester), 148.1 (HO–C=), 146.8 (H_3CO–C=), 145.6 (–HC=C– alkene carbon α to arom ring), 126.9 (–C=C– ipso), 123.4 (–HC=C– ring carbon next to methoxy group), 115.0 (–HC=CH– alkene carbon β to ipso carbon of the aromatic ring), 114.8 (HO–C=CH–), 109.3 (–HC=C_{ipso}), 74.9 (HOCH–), 64.40 (–HCOH), 64.12 (–HCOH–), 60.39 (–CH_2O–), 55.95 (epoxy carbon), 34.50 (–CH_2–COO–), 34.36 (–CH_2–CH_2O–), 31.81 (–H_2C–COH–), 31.50 (–CH_2–CH_2–CH_2–CHOH–), 29.51 (–H_2C–$CH_2CH_2CH_2$–), 29.40, 29.37, 29.32, 29.18, 29.12, 29.04, 28.63, 26.64, 25.91, 25.36, 24.98, 22.63 (–$CH_2CH_2CH_2CH_3$), 21.02 (–CH_2–CH_3), 14.18 (CH_3), 14.08 (CH_3). FD^+ MS m/z: 980.2 ($M^{+\bullet}$ C_{38} diferulate, 3.0%), 1008.9 ($M^{+\bullet}$ C_{40} diferulate,10%), 1152.6 $(M–5)^{+\bullet}$ C_{38} triferulate, 100%, 1180.6 $(M–4)^{+\bullet}$ C_{40}, triferulate 8.0%, 1214.1 $(M+1)^{+\bullet}$ C_{42}, triferulate 4%, 1274.3 $(M–5)^{+\bullet}$ C_{46} triferulate 10%.

2.4.2. Jojoba ferulate

Tetrahydroxy jojoba wax (18.30 g, 26.73 mmol), ferulic acid (20.97 g, 107.99 mmol), toluene (100 ml) and anhydrous zinc chloride (1.0 g) were placed in a dry 250 ml, 2-necked RBF that was fitted with a Dean–Stark trap and reflux condenser. The reaction mixture was stirred and heated to gentle reflux overnight. After approximately 14 h, the reaction was judged to be complete by TLC using hexanes/ethyl acetate/acetic acid, 10:5:1 as solvent and the absence of any further accumulation of condensed water in the trap. The product mixture was allowed to cool and transferred into a separatory funnel containing 100 ml of deionized water. The contents of the funnel were mixed and allowed to separate and the aqueous portion was discarded. The organic layer was washed twice more with saturated NaCl solution and dried (Na_2SO_4). Removal of solvent in vacuo give 33.10 g of the crude jojoba ferulate which was purified (VLC) in ethyl acetate-hexanes to give 27.6 g (84%) of an orange-red jojoba ferulate semisolid. A solution of the product in ethyl acetate gave UV spectral bands at 321.5 nm and at 254 nm. FTIR (KBr_{smear}) cm^{-1} values were: 3544 sh, 3422 bm (OH phenolic), 2925 vs (–CH_2– asymm stretch), 2854 s (–CH_2–, –CH_3 symm stretch), 1733 s (C=O alkyl ester), 1712 s C=O conjugated arom ester), 1632 m (–H–C=CH–), 1603 m, 1514 s (C=C arom breathing modes), 1465 m-s (–CH_2– deformation), 1431 m, 1375 m (–CH_3 deformation), 1268 s (C–C–O_2– stretch), 1208 m-s, 1157 s, 1034 m (–C–CH_2O– stretch), 983 w-m, 846 w, 817 w, 722 w. The ^1H NMR ($CDCl_3$) δ (ppm) were: 7.63 d (J = 15.9 Hz, 2H H–C=, *trans*), 7.04 d (J = 2 Hz, 3H arom ring), 6.90 d (J = 8.1 Hz, 2H *ortho* coupling, arom ring), 6.30 d (J = 15.9 Hz, 2H H–C=C–H, *trans*), 5.20 bs (OH, phenolic, 2H), 4.10 q (J = 14.3 Hz, 2H –CH_2O–), 4.02 bs (OH, phenolic 2H), 3.91 s (OCH_3, 9H), 2.25 t (J = 23.8 Hz –CH_2–, 2H), 2.02 s (6H), [1.73 bs; 1.58 bs, 1.24 bs (71H)], 0.84 t (J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ(ppm): 174.1 –OC(O)– alkyl ester, 171.2 –OC(O)-feruloyl ester, 170.8 –OC(O)– feruloyl ester, 170.7 –OC(O) feruloyl ester, 146.6 (–C=C–OH), 146.5 (–C=C–OH), 146.0 (–C=C–OH), 145.8 (–C=C–OH), 144.7 (–C=C–OCH_3), 144.6 (–C=C–OCH_3), 144.2 (–CH=C–OH_3), 144.0 (–HC=C– arom side chain α-carbon), 140.3 (–HC=C– arom side chain), 139.9 (–HC=C– arom side chain), 139.6 (–C=C– ipso), 138.5 (–C=C– ipso), 137.9 (–C=C– ipso), 136.9 (–C=C– ipso), 121.2 (–C=C–), 120.5 (–C=C–), 114.24 (–C=C–), 114.20 (–C=C–), 110.95 (–C=C–), 110.72 (–C=C–), 110.57 (–C=C–), 110.3 (–C=C–), 105.9 (–C=C–), 105.5 (–C=C–), 75.23 (–CHO–), 74.34 (–CHO–), 73.99 (–CHO–), 64.49 (–CHO–), 63.82 (–CH_2O), 56.21 (–OCH_3), 56.16 (–OCH_3), 56.02 (–OCH_3), 55.94 (–OCH_3), 50.14 (–OCH_3), 49.14 (–CH_2–CHO), 46.94 (–OCH–CH_2–), 45.36 (–CH_2–CO_2–), 38.12 (–CH_2–CHO), 38.09

(–CH_2–CHO), 34.46, (–CH_2–CH_2CH_2O–), 31.90 (CH_2–CH_2–CH_2O–), 31.28 (–CH_2–CH_2CH_3), 30.83 (–CH_2–), 29.77 (–CH_2–), 29.63 (–CH_2–), 29.46 (–CH_2–), 29.31 (–CH_2–), 29.21 (–CH_2–), 29.13 (–CH_2–), 28.73 (–CH_2–), 26.66 (–CH_2–), 26.00 (–CH_2–), 25.63 (–CH_2–), 25.40 (–CH_2–), 25.24 (–CH_2–), 25.08 (–CH_2–), 22.72 (–CH_2–), 21.12 (–CH_2–), 21.04 (–CH_2–$(CH_2)_2$–CH_3], 20.92 (–CH_2–CH_3), 19.69 (–CH_2–CH_3), 14.27 (–CH_3), 14.17 (–CH_3). The FAB$^+$ MS shows *m*/*z*: 1035.2 $(M+1)^{+\bullet}$ C_{42} diferulate 50%, 1062.6 $(M+2)^{+\bullet}$ C_{44} diferulate 40%, 1188.7 $(M+3)^{+\bullet}$ C_{40} triferulate 30%, 1213.5 ($M^{+\bullet}$ C_{42} triferulate 38%), 1242.4 $(M+1)^{+\bullet}$ C_{44} triferulate 30%, 1337.4 $(M+4)^{+\bullet}$ C_{38} tetraferulate 30%, 1364.5 $(M+3)^{+\bullet}$ C_{40} tetraferulate 28% with several unidentified fragments.

3. Results and discussion

3.1. Diepoxyjojoba derivatives

The epoxidation of jojoba oil was facile so that complete reaction was achieved in approximately 3 h. The epoxy product initially existed in two physical states: a crystalline spherical condition (minor component) and a liquid state (major component), which finally solidified on standing. Both materials had the same infrared absorption characteristics. Prominent features of the FTIR spectrum of the product were the absence of the 3008–3004 cm^{-1} (=C–H) stretch and the 1655 cm^{-1} (C=C) breathing modes usually observed in the starting material, whereas the appearance of a band at 848–844 cm^{-1} indicated the introduction of a C–O–C stretching vibration of an epoxide.

The ^{1}H NMR spectrum of the starting material shows the presence of vinylic protons (5.35 ppm) that have been replaced by a set of methine protons of the epoxy functional groups at 2.91 ppm, a multiplet resulting from neighboring methylene proton couplings. The triplet at 2.30 ppm is assignable to the methylene protons proximal to the carbonyl group, whereas the four-proton multiplet at 1.62 ppm corresponds to the methylene adjacent to the methine protons. If each of these adjacent methylene proton-set were chemically equivalent, the proton count for the multiplet would have been eight. The other set of four are therefore at higher field, overlapping with the multiplet at 1.51–1.29 ppm. Furthermore, the presence of the epoxy groups in this product was also confirmed by the ^{13}C NMR resonance at 57.31 ppm, which was absent in the starting material. The composition of the jojoba oil used in this work is listed in Table 1. A noteworthy observation in this data was the absence of a C36 component in the field desorption mass spectrum of the oil compared to earlier reports (Spencer and Plattner, 1984; Schulten et al., 1987). It had earlier been noted, however, that phenotypical differences among jojoba plants do result in variability in seed oil composition (Miwa, 1971).

Table 1
Composition of jojoba oil used as determined from FD-MS data

Carbon chain length	Composition (%)
C38	6.8
C40	35.0
C42	45.0
C44	10.8
C46	2.2

3.2. Tetrahydroxyjojoba wax

The colorless waxy tetrahydroxyjojoba derivative was obtained using mild mineral acid hydrolytic ring opening of the intermediate diepoxyjojoba ester either by a two-step process or in a one-pot reaction from the starting oil (Harry-O'kuru and Carriere, 2002; Harry-O'kuru et al., 2002). The main FTIR spectral characteristics observed for the starting oil and the tetrahydroxy derivative are shown in Fig. 1A and B. A prominent O–H stretch centered at 3405 cm^{-1} and the disappearance of the 848–844 cm^{-1} frequency of its epoxy precursor were noted. Also in contrast to the starting material, the ^{1}H NMR spectrum clearly indicates the absence of vinylic protons (5.35 ppm) and instead gives resonances at 3.89 and 3.60 ppm, multiplets resulting from coupling with the diastereotopic methylene protons that are contiguous to the four methine protons attached to hydroxylated carbons. The ^{13}C NMR spectrum also showed resonances corresponding to the primary (1°) and secondary (2°) carbons bearing oxygen atoms (64.47 ppm and 69.12, 73.96 ppm), respectively, for the single 1° and four 2° hydroxylated carbons. None of the latter four had an epoxy relationship. The MDSC of a sample of tetrahydroxyjojoba wax produced an endothermic transition during the heating (melting) cycle between −25 and 100 °C. The first

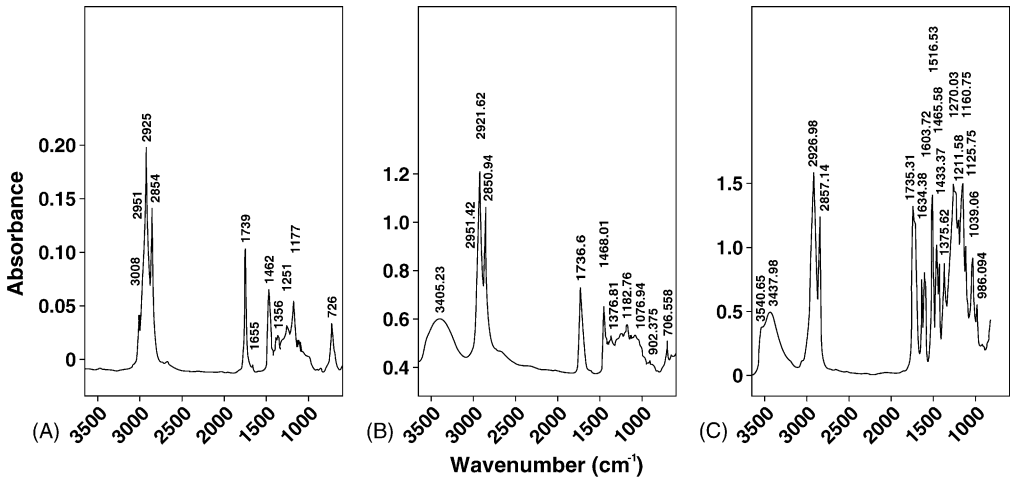

Fig. 1. FTIR spectra of jojoba oil derivatives: (A) jojoba liquid wax; (B) tetrahydroxyjojoba wax; (C) jojoba ferulate.

cycle is generally excluded because it tends to contain the thermal history of the material. The data in Table 2 show that this material starts to melt at 19 °C and is completed at 42 °C. The cycling process did not change the melting range and reorganizational (crystallization) characteristics of the material as evidenced in Fig. 2. However, as the heating and cooling cycles progressed, a 9% decrease in enthalpy (ΔH) was observed at cycle number 5. This suggests that the reorganization of the molecules may not have been 100% complete. At the end of the heating cycle, the material was cooled to −25 °C, during which an exothermic transition occurred, and thus, indicating the ability of the molecules to reorganize upon cooling. Repeated cycling produced the same transitions so that all five cycles were overlaid in Fig. 2. The observation that all five thermograms were superimposeable on each other, again indicates the level of thermal stability of this material. The MDSC data is useful in giving the melting point of the material, whereas cycling allows testing of the ability of the material to withstand freeze-thaw conditions. This kind of information is needed to characterize lipid materials for use as lubricant components. The temperature values of both transitions were similar between cycles, attesting to the extent of stability of the material under these test conditions.

Table 2
MDSC values of tetrahydroxyjojoba wax

Samples cycle number	Tetrahydroxyjojoba wax		
	T_{om}, T_{oc}	T_{pm}, T_{pc}	ΔH
1	19, 28	31, 23	81, 74
2	19, 28	31, 23	76, 73
3	19, 28	31, 23	75, 70
4	19, 28	31, 23	74, 70
5	19, 28	31, 23	74, 69

T_{om}: Onset temperature during the melting cycle, T_{oc}: Onset temperature during the crystallization cycle, T_{pm}: Peak temperature during the melting cycle, T_{pc}: Peak temperature during the crystallization cycle.

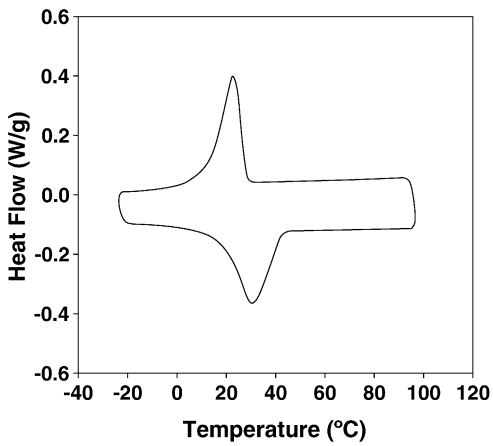

Fig. 2. Overlaid MDSC thermograms of all five cycles of the sample of tetrahydroxyjojoba wax.

Table 3A
Calculated formula masses of diepoxyjojoba derived cinnamates (FD+)

Diepoxide	Starting mass	Monoferulate	Diferulate	Triferulate	Tetraferulate
C38	592.5	786.7	980.9	1157.1	1333.3
C40	620.5	814.7	1008.9	1185.1	1361.3
C42	648.5	842.7	1036.9	1213.1	1389.3
C44	676.5	870.7	1064.9	1241.1	1417.3
C46	704.5	898.7	1092.9	1269.1	1445.3

3.3. Jojoba ferulates

The ferulates of jojoba oil are reddish semi-solids or gels that absorb in both long and short wavelength bands of the UV region of the electromagnetic spectrum, and thus, are visualized under a UV lamp without a spray reagent on TLC plates. Ferulation of the diepoxyjojoba wax under HCl or para-toluene sulfonic acid catalysis was very slow. This may be due to the two-step process of the epoxy ring opening. An initial step is protonation of the epoxy oxygen by the acid catalyst to form an oxonium ion which is then captured by the carboxyl OH of ferulic acid acting as a base. The intermediate species formed is an α-hydroxy ester of jojoba oil epoxide. A repeat of this process results in the α-dihydroxydiferulate. The dihydroxy groups could then undergo a normal condensation reaction with loss of two water molecules to form the tetraferulate. Direct esterification of the tetrahydroxyjojoba intermediate with ferulic acid required anhydrous $ZnCl_2$ as a catalyst. Use of this catalyst drastically reduced reaction time from several days with HCl to less than 14 h, and greatly simplified the work-up procedure. The FTIR spectral features of this product include absorbances at 3438 cm^{-1} for the phenolic O–H stretch; 1715–1712 cm^{-1} stretching vibration of the conjugated ester C=O; the1604, 1516 cm^{-1} stretching vibrations of the aromatic and alkene H–C= and the 1634 cm^{-1} of the C=C breathing modes of the vinylic and aromatic systems, Fig. 1C. Acetylation of the phenolic OHs of a sample of the product (not pointed out earlier) resulted in an expected additional C=O stretching mode at 1767 cm^{-1} because of the larger force constant of the phenoxy acetate.

The ^{13}C NMR spectrum confirmed esterification of the hydroxyl functions with ferulic acid by the presence of three new ester functionalities resulting in additional low field resonances at 171.2, 170.8 and 170.7 ppm for the conjugated esters; the phenolic OH carbons are at 146.6, 146.5, 146.0 ppm. The aromatic carbons bearing methoxy groups are observed at 145.8, 144.7, 144.6 ppm; the vinylic carbons α to the aromatic ring are at 144.3, 144.0, 139.9 ppm; the aromatc ipso carbons at 139.6, 138.5, 137.9 and 136.9 ppm; the unsubstituted aromatic carbon proximal to the methoxy group is at 121.2 ppm; the ring carbon α to the phenolic OH was observed at 120.5 ppm, whereas the aromatic carbon α to C_{ipso} was at 114.24 ppm. The alkene carbon distal to the aromatic ring resonated at 114.2 ppm. The multiplicity of carbon lines observed in the ^{13}C NMR of the ferulates derived from tetrahydroxy material was expected considering the inevitable steric effects produced on segments of the alkyl chain by the substituents and vice versa. The resonance frequency of the –OC=O of the alkyl ester, however, remained unaffected because it is too far removed from any of the substituents. For a better understanding of the generated products in these reactions, Tables 3A and 3B give

Table 3B
Calculated formula masses of tetrahydroxyjojoba derived cinnamates (FAB+)

Tetrahydroxy	Starting mass	Monoferulate	Diferulate	Triferulate	Tetraferulate
C38	628.5	804.7	980.9	1157.1	1333.3
C40	656.5	832.7	1008.9	1185.1	1361.3
C42	684.5	860.7	1036.9	1213.1	1389.3
C44	712.5	888.7	1064.9	1241.1	1417.3
C46	740.5	916.7	1092.9	1269.1	1445.3

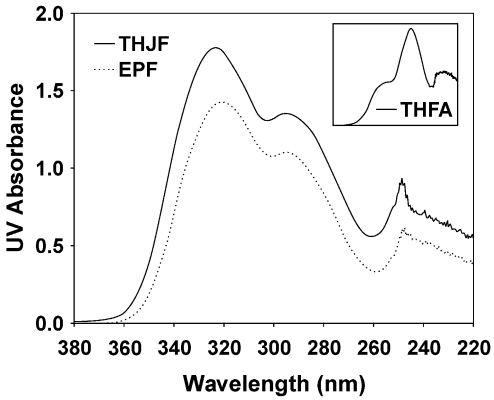

Fig. 3. Overlay of UV spectra of ferulates of the: (A) tetrahydroxy derivative, THJF, and (B) epoxy derivative, EPF.

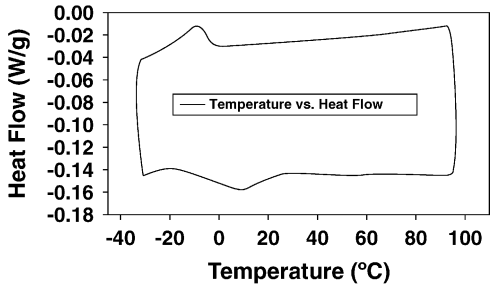

Fig. 4. DSC thermograms of all five cycles of the sample of jojoba ferulate.

the calculated masses of the various cinnamates possible from the epoxide and the tetrahydroxy starting materials. The FD^+ MS spectrum of the product from the epoxy starting material indicated formation of small amounts of diferulate molecular ions of C_{38} (3.0%) and C_{40} (10.0%). A base peak of mass ion 1152.6 corresponding to C_{38} triferulate was observed in addition to mass ions 1180.6, 1214.1, and 1274.3 attributable to the triferulates of C_{40}, C_{42} and C_{46}, respectively. This explains the observed ^{13}C NMR resonance at 55.95 ppm characteristic of epoxide carbon(s) in the spectrum of this product as a result of incomplete ferulation. The only epoxy ester that seemed unreactive under these experimental conditions was the C_{44} component. The tetrahydroxy ester, on the other hand, reacted readily giving various amounts of the di- to the tetraferulates of C_{38}–C_{46} as shown by the observed fragmentation patterns in the mass spectra.

The strong UV-absorption spectra of jojoba cinnamates are shown in Fig. 3. The ferulates derived from the tetrahydroxyjojoba wax and from the diepoxyjojoba wax exhibit the same strong UV-absorption characteristics at very low concentrations. A notable behavior observed in these cinnamates is that acetylation of the phenolic hydroxyl groups of the ferulate leads to a hypsochromic reversal of the UV-absorption intensity pattern seen in the unacetylated ferulates. This intensity blue-shift of the jojobaferuloyl acetate, THFA, favors the shorter wavelength band (280 nm) as shown in the insert of Fig. 3. These observations support the proposed use of these cinnamates as flexible and efficient UV-filter materials because they could be tailored to the needs of specific applications.

The MDSC of jojoba ferulate (Fig. 4) showed a definite thermal property change from the tetrahydroxy precursor. The melting temperature of the ferulate is much lower than that of the tetrahydroxy wax and the shape of the peak is broader. The transition temperature during the melting cycle of the ferulate started at −15 °C and ended at 22 °C with a peak temperature at 10 °C, whereas the tetrahydroxy wax started at 19 °C and ended at 42 °C and peaked at 31 °C (Table 2). The five cycles data indicate a stable ferulate similar to the tetrahydroxyjojoba wax. The endothermic transition of the ferulate material showed similar ΔH values as the exothermic (crystallization) enthalpy. The peak temperatures of the ferulate were 10.3 °C for the melting transition and −9.2 °C for the crystallization transition. This indicates a difference in the ferulate relative to the tetrahydroxy where the peak temperatures were 31 and 23 °C, respectively. The ΔH values for the two compounds showed tetrahydroxy wax to be much more organized with an average value of 77 J/g than the ferulate with 7 J/g. Because of its lower crystallization temperature and very low ΔH, it is conceivable that a formulation containing appropriate amounts of both the ferulate and tetrahydroxy wax components would form eutectics having much lower melt temperatures, that is, the product(s) would remain liquid over a broad range of temperatures. Such a material would exhibit improved skin protectant qualities as a result of the synergistic effect arising from infusion of the emollience property of the tetrahydroxyjojoba wax into the UV absorbing behavior of jojoba ferulates in the formulation.

4. Conclusions

Jojoba oil was modified by chemical functionalization of its olefinic bonds to the epoxides that were subsequently quantitatively ring-opened to the tetrahydroxyjojoba wax, a colorless, low-temperature melting solid. Direct esterification of the secondary hydroxyl functional groups of the tetrahydroxyjojoba wax with 4-hydroxy-3-methoxycinnamic acid gave the 4-hydroxy-3-methoxycinnamates. These cinnamates are also obtained by ring opening of jojobadiepoxides with ferulic acid and are excellent UV radiation absorbers, and therefore, are very attractive as UV-filter sources.

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