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ORIGINAL PAPER

Synthesis and Characterization of Soyamide Ferulate

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Abstract Ferulic acid (4-hydroxy-3-methoxycinnamic acid) is a phytochemical antioxidant that is widely distributed throughout the plant kingdom. Cinnamic acid derivatives are used as biobased ultraviolet (UV) absorbers in sunscreen formulations. Soybean oil ferulate, a biobased UV absorber, was synthesized by reacting soyamide with ferulic acid. The resulting product was characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, and gel permeation chromatography (GPC). Spectroscopic studies measured the soyamide-based ferulate maximum absorbance at 327 nm with a molar extinction coefficient of 19,705 L mol^{-1} cm^{-1}. Soyamide ferulate has potential to be used in coatings.

Keywords Vegetable oil · Soyamide · Ferulate · UV absorber

Introduction

Vegetable oil-containing crops are gaining considerable attention as renewable, environmentally responsible, nontoxic, biodegradable, and relatively inexpensive resources for monomer derivatives and polymer synthesis [1]. Commercially, vegetable oils are modified by various methods such as transesterification, amidation, maleinization, epoxidation, and acrylation to convert the triglycerides into useful derivatives [2]. Methyl esters of fatty acids (biodiesel) obtained via transesterification of vegetable oils with methanol are being utilized as a petroleum diesel substitute [3]. Epoxidized soybean oil is used as a plasticizer and precursor for the synthesis of composites [1]. Vegetable oil macromonomers (VOMMs) are novel derivatives that have been developed as viable comonomers for latex synthesis [4]. Of the many examples for biobased raw material utilization, it is the high-value added chemistries that are critical for continued research, development, and reduction to practice. Additives are traditionally incorporated in low concentrations that provide specific but crucial material functions, and are therefore high-value added materials. The research described herein focuses on the synthesis, characterization, and evaluation of biobased derivatives specifically designed to be ultraviolet light absorbers (UVAs) as protective additives for coatings.

UVAs help reduce the rates of photodegradation in materials. All organic materials degrade during natural exposure and sunlight accelerates polymer degradation via photo-oxidation. To extend the longevity of polymers and coatings, it is essential to create materials with improved weathering properties [5]. Sunlight is also detrimental to substrates such as wood as it generates free radicals that result in discoloration, weathering, and cracking [6]. Polymeric and wood substrates are often protected from the effects of outdoor weathering by UV stabilized coatings [7]. UV light stabilizers employed in coatings are broadly classified into UVAs and hindered amine light stabilizers (HALS). UVAs, for example, 2-hydroxyphenyl benzotriazole, absorb frequency specific UV light energy and dissipate absorbed energy without affecting the matrix polymer; whereas HALS, for example, 2,2,6,6-tetramethyl piperidine, produces nitroxyl radicals which couple with alkyl radicals to inhibit the degradation of polymers [8].

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Ferulic acid (4-hydroxy-3-methoxycinnamic acid) is a highly abundant, phytochemical antioxidant located in plant cell walls, for example, wheat contains 50–500 μg g^{-1} of ferulic acid [9]. Harry-O’kuru et al. [10] synthesized jojoba oil ferulates that exhibited UV absorbing properties. Compton and Laszlo [11] synthesized ferulyl-substituted acylglycerols for use as UV absorbers in sunscreen formulations by transesterifying ethyl ferulate with soybean oil. Compton et al. [12] also enzymatically reacted ferulic acid with soybean oil. The synthesis of vegetable oil ferulates as potential UV absorbers is an attractive alternative to commercial UV absorbers that are typically derived from petroleum.

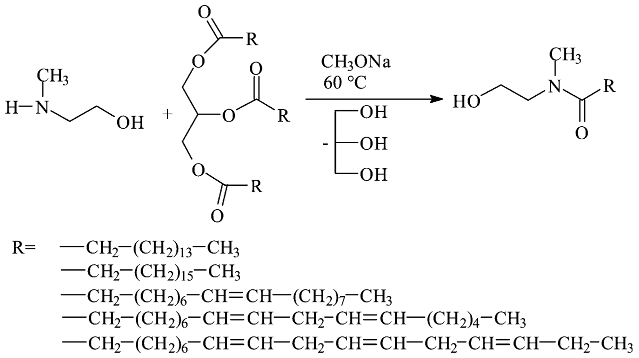
Experimental Procedures

Materials

Soybean oil was purchased from the Alnor Oil Company. *N*-methyl ethanolamine and sodium methoxide were procured from Acros Organics, while ferulic acid (99%) was purchased from the Aldrich Chemical Company. Sulfuric acid, toluene, ethyl acetate, methanol, and anhydrous magnesium sulfate were purchased from Fischer Scientific. All raw materials were used as received, except for toluene which was dried using anhydrous magnesium sulfate or molecular sieves. Soyamide was synthesized in our laboratory.

Soyamide Synthesis

A 1,000-mL three-neck flask equipped with condenser, mechanical stirrer, and nitrogen purge was charged with 500 g soybean oil. The oil was heated to 60 °C, and sodium methoxide (50 g, 25% solution in methanol) and *N*-methyl ethanolamine (125.46 g) were added to the flask. The reaction was monitored via FTIR by following the disappearance of the ester peak (1,746 cm^{-1}) and appearance of the amide peak (1,627 cm^{-1}). The product was washed with brine solution to remove glycerol and excess *N*-methyl ethanolamine. The soyamide was dried with magnesium sulfate and filtered (Scheme 1, yield 90%), and exhibited a hydroxyl number of 135 (ASTM D 4274-94, Test method C). The average fatty acid composition for soybean oil is reported as being 6.00% linolenic (C18:3), 54.00% linoleic (C18:2), 24.00% oleic (C18:1), 5.00% stearic (C18), and 11.00% palmitic (C16) fatty acids [1]. Based on this average fatty acid composition, soyamide possesses a molecular weight of 335.37 while the hydroxyl value provides a molecular weight of 415 (ASTM D 1899).



Scheme 1 Soyamide synthesis from soybean oil

Soyamide Ferulate Synthesis

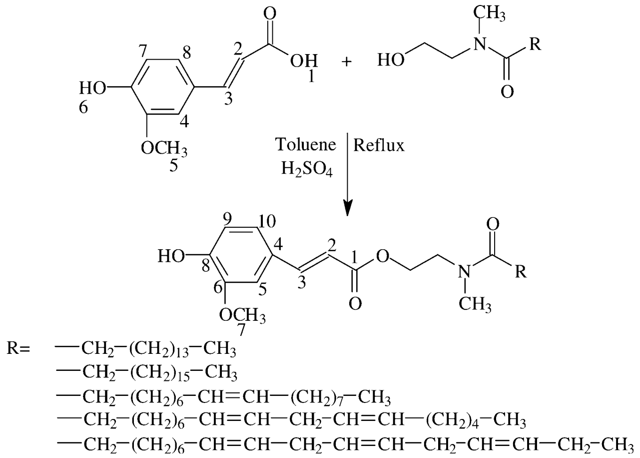
Ferulic acid (15.01 g, 77.37 mmol), soyamide (32.10 g, 77.35 mmol), and toluene (200 mL) were placed in a dry, three-neck, 500-mL round-bottom flask fitted with Dean–Stark trap, reflux condenser, and nitrogen purge. The reaction mixture was heated to 80 °C and sulfuric acid (0.6014 g) was added. The contents were refluxed for 48 h, which is less than the reaction times reported earlier [10, 11]. Most of the toluene was removed under reduced pressure and ethyl acetate ($\sim$200 mL) was added. The flask contents were transferred to a separatory funnel and washed three times with 10% brine solution containing small amounts of sodium bicarbonate to remove unreacted ferulic acid (Scheme 2). The organic phase was dried over anhydrous magnesium sulfate and the solvents were removed under reduced pressure to yield soyamide ferulate (88% yield). Ferulic acid was determined to have an acid value of 337 mg KOH g^{-1} via ASTM D 1639-90, which was higher than the theoretical value of 289 (based on carboxyl group only), and was attributed to the partial contribution from the phenolic OH. Using the same method, soyamide ferulate was determined to have an acid value of 39 mg KOH g^{-1}. The calculated molar mass of soyamide suggests that soyamide ferulate has a molecular weight of 511.37. Hydroxyl value calculations infer that the soyamide ferulate weight was 591, which is close to the value of 636 obtained by GPC.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra were obtained with a Digilab FTIR spectrometer over a frequency range of 600–4,000 cm^{-1}. The samples were analyzed as thin films over sodium chloride discs.

Nuclear Magnetic Resonance Spectroscopy

Proton and carbon spectra were obtained using a Varian mercury nuclear magnetic resonance (NMR) spectrometer operating at a frequency of 300.13 and 75.5 MHz for



Scheme 2 Soyamide ferulate synthesis

proton and carbon NMR spectroscopy, respectively. Typical ^{1}H-NMR acquisition parameters were as follows: recycle delay of 1 s, 7.1 μs pulse width corresponding to a 45° flip angle, and acquisition time of 2 s. ^{13}C-NMR acquisition parameters were: 1 s recycle delay, 7.8 μs pulse width corresponding to 45° flip angle, and acquisition time of 1.8 s. All chemical shifts (indicated as δ ppm) were referenced either automatically by the software (VNMR 6.1C) or manually using the resonance frequency of the deuterated solvent (DMSO-*d*$_6$ or CDCl$_3$). An NMR spectrum of soybean oil was obtained in CDCl$_3$, while soyamide was analyzed in CDCl$_3$ and DMSO-*d*$_6$ (as soyamide did not show an alcoholic OH proton peak in CDCl$_3$ singularly). Ferulic acid and soyamide ferulate were analyzed in DMSO-*d*$_6$ as ferulic acid is insoluble in CDCl$_3$.

The average fatty acid composition for soybean oil was reported as 6.00% linolenic (C18:3), 54.00% linoleic (C18:2), 24.00% oleic (C18:1), 5.00% stearic (C18), and 11.00% palmitic (C16) fatty acids [1]. The diverse fatty acid composition results in complicated NMR spectra of soybean oil and its derivatives. As the terminal methyl group protons overlap with the linolenic acid protons, it is difficult to estimate the exact number of protons via integration, and only the chemical shifts resulting from the change in functional groups have been used as evidence for structure determination.

NMR spectral data: Fig. 2b soyamide (^{1}H CDCl$_3$): δ 7.26 (imp, CDCl$_3$), 5.35 (m, ~4H, –C*H*=C*H*–), 3.77 (t, 2H, –N–CH$_2$–C*H*$_2$–OH), 3.55 (t, 2H, –N–CH$_2$–C*H*$_2$–OH), 3.06 (s, 3H, –N–C*H*$_3$), 2.96 (s, –N–C*H*$_3$), 2.77 (t, 2H, –CH=CH–C*H*$_2$–CH=CH–), 2.33 (m, ~2H, –N–CO–C*H*$_2$–), 2.03 (m, ~4H, –CH=CH–C*H*$_2$–), 1.63 (m, ~2H, –N–CO–CH$_2$–C*H*$_2$–), 1.28 (m, ~20H, –C*H*$_2$–), 0.97 (t, –CH=CH–CH$_2$–C*H*$_3$) and 0.89 (t, 3H, –CH$_2$–CH$_2$–C*H*$_3$) and Fig. 2c soyamide (^{1}H DMSO-*d*$_6$): δ 5.30 (m, ~4H, –C*H*=C*H*–), 4.75–4.58 (s, 1H, –N–CH$_2$–CH$_2$–O*H*), 3.47 (dt, 2H, –N–CH$_2$–C*H*$_2$–OH), 3.31 (–N–C*H*$_2$–CH$_2$–OH and HOD), 2.95 (s, 3H, –N–C*H*$_3$), 2.77 (s, 3H, –N–C*H*$_3$), 2.71 (t, 2H, –CH=CH–C*H*$_2$–CH=CH–), 2.48 (imp, DMSO-*d*$_6$), 2.25 (tt, ~4H, –N–CO–C*H*$_2$–), 1.98 (m, ~4H, –CH=CH–C*H*$_2$–), 1.44 (m, ~4H, –N–CO–CH$_2$–C*H*$_2$–), 1.23 (m, ~20H, –C*H*$_2$–), 0.90 (t, –CH=CH–CH$_2$–C*H*$_3$), 0.83 (t, 3H, –CH$_2$–C*H*$_3$).

NMR spectral data: soyamide (^{1}H DMSO-*d*$_6$) at 100 °C: δ 5.33 (m, ~4H, –C*H*=C*H*–), 4.32 (bs, 1H, –N–CH$_2$–CH$_2$–O*H*), 3.50 (t, 2H, –N–CH$_2$–C*H*$_2$–OH), 3.34 (t, 2H, –N–C*H*$_2$–CH$_2$–OH), 2.95 (bs, ~6H, –N–C*H*$_3$), 2.74 (t, 2H, –CH=CH–C*H*$_2$–CH=CH–), 2.48 (imp, DMSO-*d*$_6$), 2.26 (t, 2H, –N–CO–C*H*$_2$–), 2.01 (m, ~4H, –CH=CH–C*H*$_2$–), 1.51 (m, ~4H, –N–CO–CH$_2$–C*H*$_2$–), 1.27 (m, ~20H, –C*H*$_2$–), 0.94 (t, –CH=CH–CH$_2$–C*H*$_3$), 0.84 (t, 3H, –CH$_2$–C*H*$_3$).

NMR spectral data of soyamide (^{13}C CDCl$_3$): δ 174.70 (–N–*C*O–CH$_2$–), 174.67 (–N–*C*O–CH$_2$–), 174.13 (–N–*C*O–CH$_2$–), 174.08 (–N–*C*O–CH$_2$–), 131.76–126.99 (–*C*H=*C*H–), 77.20 (CDCl$_3$), 60.72 (–N–CH$_2$–*C*H$_2$–OH), 59.40 (–N–CH$_2$–*C*H$_2$–OH), 52.02 (–N–*C*H$_2$–CH$_2$–OH), 50.86 (–N–*C*H$_2$–CH$_2$–OH), 36.69 (–N–*C*H$_3$), 33.57 (–N–CO–*C*H$_2$–), 33.50 (–N–CO–*C*H$_2$–), 33.07 (–N–CO–*C*H$_2$–), 31.83 (*ω*3 –*C*H$_2$–), 31.81 (*ω*3 –*C*H$_2$–), 31.41 (*ω*3 –*C*H$_2$–), 29.66–29.08 (CH=CH–*C*H$_2$–, –*C*H$_2$–), 27.10 (–CH=CH–*C*H$_2$–CH=CH–), 27.08 (–CH=CH–*C*H$_2$–CH=CH–), 25.51–24.90 (–N–CO–CH$_2$–*C*H$_2$–), 22.59 (*ω*2 –*C*H$_2$–), 22.47 (*ω*2 –*C*H$_2$–), 14.18 (*ω*1 –*C*H$_3$), 14.02 (*ω*1 –*C*H$_3$) and 13.98 (*ω*1 –*C*H$_3$).

NMR spectral data: Fig. 3 soyamide (^{13}C DMSO-*d*$_6$): δ 172.41 (–N–*C*O–CH$_2$–), 172.14 (–N–*C*O–CH$_2$–), 131.74–127.26 (–*C*H=*C*H–), 59.28 (–N–CH$_2$–*C*H$_2$–OH), 59.06 (–N–CH$_2$–*C*H$_2$–OH), 51.74 (–N–*C*H$_2$–CH$_2$–OH), 50.21 (–N–*C*H$_2$–CH$_2$–OH), 36.51 (–N–*C*H$_3$), 33.40 (–N–CO–*C*H$_2$–), 33.08 (–N–CO–*C*H$_2$–), 32.58 (–N–CO–*C*H$_2$), 31.88 (*ω*3 –*C*H$_2$–), 31.86 (*ω*3 –*C*H$_2$–), 31.43 (*ω*3 –*C*H$_2$–), 29.70–29.21 (CH=CH–*C*H$_2$–, –*C*H$_2$–), 27.14 (–CH=CH–*C*H$_2$–CH=CH–), 27.08 (–CH=CH–*C*H$_2$–CH=CH–), 25.58–25.04 (–N–CO–CH$_2$–*C*H$_2$–), 22.64 (*ω*2 –*C*H$_2$–), 22.50 (*ω*2 –*C*H$_2$–), 14.37 (*ω*1 –*C*H$_3$) and 14.16 (*ω*1 –*C*H$_3$).

NMR spectral data: Fig. 5b soyamide based ferulate (^{1}H DMSO-*d*$_6$) at ambient temperature: δ 9.59 (bs, 1H, aromatic, 6-*H*), 7.51 (d, *J* = 15.8 Hz, 1H, Ph–C*H*=CH–, *trans*), 7.27 (s, 1H, aromatic ring, 4-*H*), 7.07 (d, *J* = 7.9 Hz, 1H, aromatic ring, 8-*H*), 6.76 (d, *J* = 7.9 Hz, 1H, aromatic ring, 7-*H*), 6.41 (d, *J* = 15.8 Hz, 1H, Ph–CH=C*H*, *trans*), 5.28 (m, ~4H, –C*H*=C*H*–), 4.22 (dt, 2H, –N–CH$_2$–C*H*$_2$–O–CO–), 3.79 (s, 3H, Ph–OC*H*$_3$), 3.55 (t, 2H, –N–C*H*$_2$–CH$_2$–O–CO–), 3.31 (HOD), 2.99 (s, 3H, –N–C*H*$_3$), 2.81 (–N–C*H*$_3$), 2.76 (m, ~2H, –CH=CH–C*H*$_2$–CH=CH–), 2.48 b (imp, DMSO-*d*$_6$), 2.23 (m, ~2H, –N–CO–C*H*$_2$–), 1.97 (t, ~4H, –CH=CH–C*H*$_2$–), 1.44 (m, ~2H, –N–CO–CH$_2$–C*H*$_2$–), 1.21 (m, ~20H, –C*H*$_2$–), 0.89 (t, –CH=CH–CH$_2$–C*H*$_3$), 0.82 (t, 3H, –CH$_2$–CH$_2$–C*H*$_3$) (H labeled as shown in

Scheme 2) and Fig. 5c soyamide based ferulate (^{1}H DMSO-d_6) at 100 °C: δ 9.10 (bs, 1H, aromatic, 6-*H*), 7.53 (d, *J* = 15.8 Hz, 1H, Ph–C*H*=CH–, *trans*), 7.22 (s, 1H, aromatic ring, 4-*H*), 7.06 (d, *J* = 7.9 Hz, 1H, aromatic ring, 8-*H*), 6.80 (d, *J* = 7.9 Hz, 1H, aromatic ring, 7-*H*), 6.33 (d, *J* = 15.8 Hz, 1H, Ph–CH=C*H*, *trans*), 5.32 (m, ~4H, –C*H*=C*H*–), 4.25 (t, 2H, –N–CH$_2$–C*H*$_2$–O–CO–), 3.83 (s, 3H, Ph–OC*H*$_3$), 3.59 (t, 2H, –N–C*H*$_2$–CH$_2$–O–CO–), 2.95 (bs, ~6H, –N–C*H*$_3$), 2.73 (t, 2H, –CH=CH–C*H*$_2$–CH=CH–), 2.48 (imp, DMSO-d_6), 2.27 (dt, ~4H, –N–CO–C*H*$_2$–), 2.01 (t, ~4H, –CH=CH–C*H*$_2$–), 1.51 (m, ~2H, –N–CO–CH$_2$–C*H*$_2$–), 1.25 (m, ~20H, –C*H*$_2$–), 0.93 (t, –CH=CH–CH$_2$–C*H*$_3$) 0.86 (t, 3H, –CH$_2$–CH$_2$–C*H*$_3$) (H labeled as shown in Scheme 2).

NMR spectral data of soyamide based ferulate (^{13}C DMSO-d_6): δ 172.23 (N–*C*O–CH$_2$–), 171.98 (N–*C*O–CH$_2$–), 166.47 (CH=CH–*C*OO–CH$_2$–), 166.38 (–CH=CH–*C*OO–CH$_2$–), 149.52 (aromatic, *C*-6), 147.93 (aromatic, *C*-8), 145.54 (Ph–*C*H=CH–COO–CH$_2$–), 131.45–126.95 (–*C*H=*C*H–), 125.52 (aromatic, *C*-4), 123.16 (aromatic, *C*-10), 115.47 (aromatic, *C*-9), 113.81 (aromatic, *C*-5), 111.19 (Ph–CH=*C*H–CO–O–), 111.12 (Ph–CH=*C*H–CO–O–), 61.33 (–N–CH$_2$–*C*H$_2$–O–CO–), 61.07 (–N–CH$_2$ –*C*H$_2$–O–CO–), 55.64 (Ph–O*C*H$_3$), 47.83 (–N–*C*H$_2$–CH$_2$–O–CO–), 46.13 (–N–*C*H$_2$–CH$_2$–O–CO–), 35.88 (–N–*C*H$_3$), 32.94 (–N–CO–*C*H$_2$–), 32.55 (–N–CO–*C*H$_2$–), 31.93 (ω3 –*C*H$_2$–), 31.35 (ω3 –*C*H$_2$–), 30.94 (ω3 –*C*H$_2$–), 29.30–28.51 (–CH=CH–*C*H$_2$–, –*C*H$_2$–), 26.62 (–CH=CH–*C*H$_2$–CH=CH–), 25.19–24.58 (–N–CO–CH$_2$–*C*H$_2$–), 22.15 (ω2 –*C*H$_2$–), 22.03 (ω2 –*C*H$_2$–), 13.88 (ω1 –*C*H$_3$) (carbons labeled as shown in Scheme 2).

Gel Permeation Chromatography

Gel permeation chromatography (GPC) analysis was performed using a chromatographic system consisting of a Waters 515 HPLC pump, a Waters 2414 refractive index (RI) detector, and a Polypore 300 × 7.5 mm column (Polymer Laboratories). Tetrahydrofuran (THF) was used as the mobile phase at 1 mL min^{-1} at 40 °C using toluene as the flow marker. The RI detector was calibrated using poly(methyl methacrylate) standards purchased from Polymer Laboratories.

UV–VIS Spectroscopy

UV–vis spectra were recorded on a Cary 500 Scan UV–VIS–NIR spectrophotometer at ambient temperature. The samples were dissolved in methanol for analysis. Plastibrand® disposable cuvettes (1.5 mL volume) having a detectable wavelength range of 220–900 nm and 10 mm standard light path length were used to perform the spectroscopic test.

Results and Discussion

Soyamide Synthesis

Figure 1 is the Fourier transform infrared (FTIR) spectra of soybean oil and soyamide. Characteristic bands of soybean oil were observed at 3,009, 2,926, 2,855, 1,746, 1,462, 1,164, and 723 cm^{-1} resulting from C–H stretching of CH=CH, C–H asymmetric stretching of CH$_2$, C–H symmetric stretching of CH$_2$, C=O stretching of ester (glyceride), CH$_2$ scissoring, O–C–C stretching of ester, and CH$_2$ rocking, respectively [1]. The soyamide spectrum shows new bands at 3,399 and 1,627 cm^{-1} attributed to OH (H-bonded) stretching, and C=O stretching of amide, respectively. The disappearance of peaks at 1,746 and 1,164 cm^{-1} and appearance of peaks at 3,399 and 1,627 cm^{-1} confirm soyamide formation from the coreaction with soybean oil.

Figure 2 is the ^{1}H-NMR spectra of soybean oil and soyamide. The ^{1}H-NMR spectrum of soybean oil shows the glycerol methine proton at δ 5.27 ppm and glycerol methylene protons at δ 4.29–4.14 ppm [1]. Lack of these signals in the soyamide spectrum and the appearance of new signals at δ 3.77, 3.55, and 3.06 ppm due to methylene protons adjacent to the –OH group of –N–CH$_2$–C*H*$_2$–OH, methylene protons adjacent to nitrogen of –N–C*H*$_2$–CH$_2$–OH, and methyl protons of –N–C*H*$_3$ verify soyamide synthesis from soybean oil. Signals noted at δ 3.66, 3.47, 3.26, and 2.96 ppm were attributed to H-bonding interactions, resonating interactions, or the presence of impurities. Two sets of methyl proton signals are observed in dimethyl formamide due to rotation being restricted by resonance

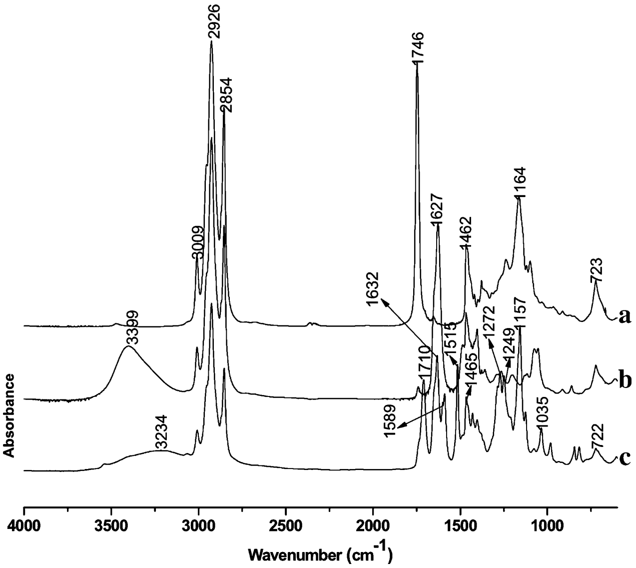


Fig. 1 FTIR spectra of *a* soybean oil, *b* soyamide and **c** soyamide ferulate

and these two sets of proton signals exhibited one signal at about 130 °C [13]. Since the alcoholic proton signal of –N–CH$_2$–CH$_2$–O*H* was not observed clearly in the spectrum of soyamide dissolved in CDCl$_3$, soyamide was analyzed via ^{1}H NMR in DMSO-*d*$_6$, and the alcoholic proton was observed at δ 4.75–4.58 ppm (Fig. 2c). ^{1}H-NMR spectrum of soyamide obtained at 100 °C showed a broad alcoholic proton peak for –N–CH$_2$–CH$_2$–O*H* at δ 4.32 ppm, methylene proton adjacent to OH of –N–CH$_2$–C*H*$_2$–OH at δ 3.50 ppm, methylene proton adjacent to nitrogen of –N–C*H*$_2$–CH$_2$–OH at δ 3.34 ppm, and methyl proton of –N–C*H*$_3$ at δ 2.95 ppm. Proton signals for –N–CH$_2$–C*H*$_2$–OH, –N–C*H*$_2$–CH$_2$–OH, and –N–C*H*$_3$ of soyamide in DMSO-*d*$_6$ at ambient temperature and 100 °C suggests the probability of the H-bonding and other interactions. Integration of the ^{1}H-NMR spectrum (in DMSO-*d*$_6$) at 100 °C showed that the ratio of protons –N–C*H*$_2$–C*H*$_2$–OH to terminal protons –CH$_2$–C*H*$_3$ was 1.31 (expected value 1.33). The disappearance of glycerol methine and methylene protons and appearance of –N–CH$_2$–C*H*$_2$–OH, –N–C*H*$_2$–CH$_2$–OH and –N–C*H*$_3$ protons attest to the formation of soyamide from soybean oil. Further confirmation of the synthesis results via ^{13}C-NMR spectra of soybean oil and soyamide in CDCl$_3$. The glycerol methine and methylene carbons revealed in the soybean oil spectrum at δ 68.84 and 61.97 ppm, respectively, are no longer observed in the ^{13}C-NMR spectrum of soyamide; additionally, new signals were noted at δ 60.72–59.40 ppm for methylene carbon attached to OH of –N–CH$_2$–*C*H$_2$–OH, at δ 52.02–50.86 ppm for methylene carbon attached to nitrogen of –N–*C*H$_2$–CH$_2$–OH, and at δ 36.69 ppm for methyl carbon of –N–*C*H$_3$. Methylene carbon bonded to OH of –N–CH$_2$–*C*H$_2$–OH was observed at δ 59.28–59.06 ppm, methylene carbon bonded to nitrogen of –N–*C*H$_2$–CH$_2$–OH at δ 51.74–50.21 ppm, and methyl carbon of N–*C*H$_3$ at δ 36.51 ppm were noticed in the spectrum of soyamide dissolved in DMSO-*d*$_6$ (Fig. 3).

Gel permeation chromatography was used to illustrate the soyamide synthesis from soybean oil (Fig. 4). It is observed that soybean oil eluted at 16.90 min while soyamide eluted at 18.51 min. The toluene flow marker eluted at 21.17 min. A small peak that eluted between 16 and 18 min can be attributed to unreacted soybean oil, and is consistent with the lower than expected hydroxyl value of soyamide.

Soyamide Ferulate Synthesis

The FTIR spectrum of soyamide ferulate is shown in Fig. 1. The band at 3,399 cm^{-1} for soyamide OH (H-bonded) is absent in the ferulate spectrum, while new bands are noted in the ferulate spectra at 3,234 cm^{-1} (O–H stretching, phenolic), 1,710 cm^{-1} (C=O stretching of ferulate ester), 1,589 and 1,515 cm^{-1} (C=C breathing of benzene ring), 1,429 cm^{-1} (C–H bending of CH$_3$), 1,272 and 1,249 cm^{-1} [C–C(=O)–O stretching of unsaturated ester], 1,157 and 1,035 cm^{-1} (O–C–C stretching of ester), 982 cm^{-1} (C–H bending of CH=CH of ferulic acid), and 848 and 825 cm^{-1} (C–H bending of aromatic ring, out of plane) [10]. The data confirms the ferulate ester synthesis from soyamide.

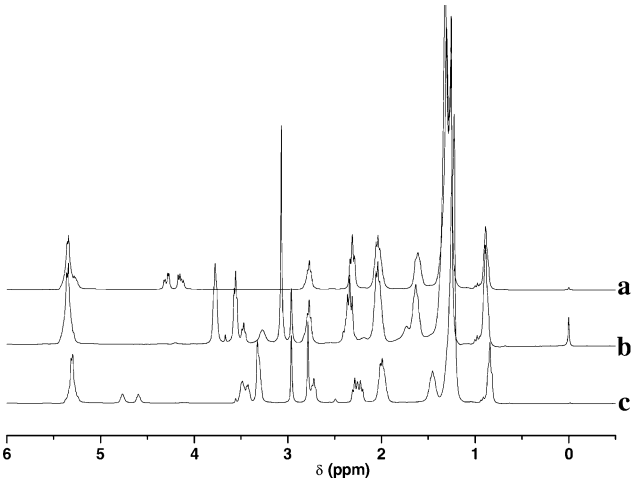


Fig. 2 ^{1}H-NMR spectra of *a* soybean oil, *b* soyamide in CDCl$_3$ and *c* soyamide in DMSO-*d*$_6$ at ambient temperature

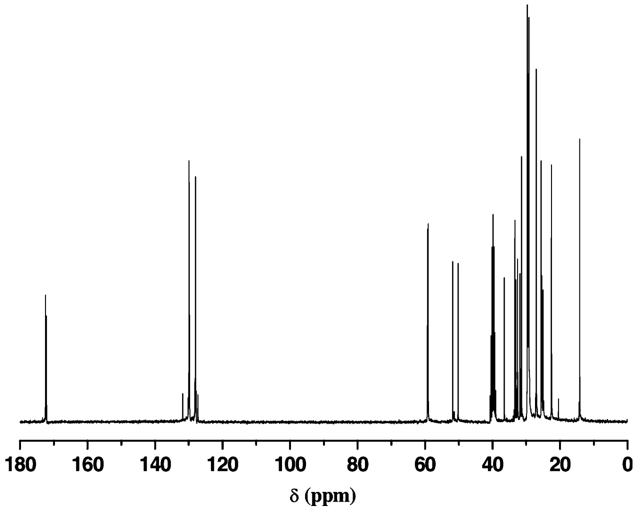


Fig. 3 ^{13}C-NMR spectrum of soyamide in DMSO-*d*$_6$ at ambient temperature

^{1}H-NMR spectra of ferulic acid and soyamide ferulate are shown in Fig. 5. Carboxylic acid proton of –CH=CH–COO*H* observed at δ 12.15 ppm in the ferulic acid spectrum was absent in the ferulate spectrum. Concomitantly, new signals were observed at δ 4.26 ppm for methylene proton adjacent to ester oxygen of –N–CH$_2$–C*H*$_2$–O–CO–, at δ 3.55 ppm for methylene proton adjacent to nitrogen of –N–C*H*$_2$–CH$_2$–O–CO–, and at δ 2.99 ppm for the methyl

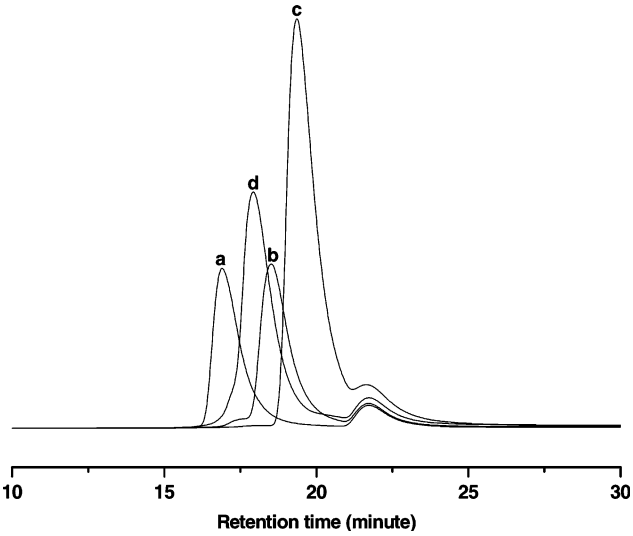


Fig. 4 GPC profiles of *a* soybean oil, *b* soyamide, *c* ferulic acid and *d* soyamide ferulate

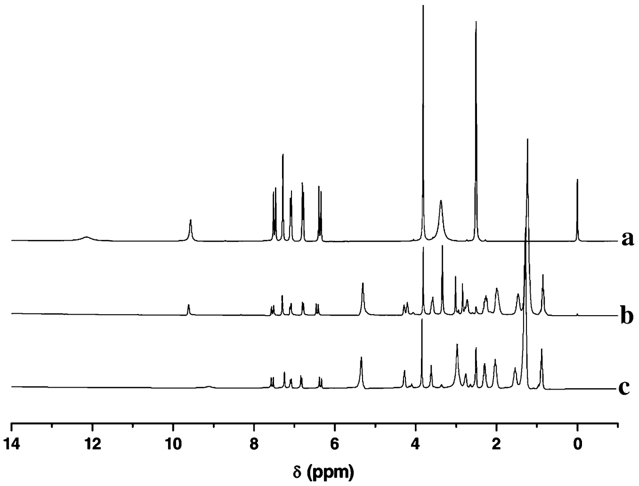


Fig. 5 ^{1}H-NMR spectra of *a* ferulic acid, *b* soyamide ferulate at ambient temperature and *c* soyamide at 100 °C temperature. The spectra were determined in DMSO-d_6

protons of –N–CH_3. The ^{1}H-NMR spectrum of soyamide ferulate analyzed at 100 °C, indicated that the signals at 4.26 and 4.18 ppm had merged into a single peak at δ 4.25 ppm (Fig. 5c). The shift of the methylene proton peak of –N–CH$_2$–CH_2–OH at δ 3.50 ppm in soyamide to δ 4.25 ppm of –N–CH$_2$–CH_2–O–CO in soyamide ferulate, and disappearance of the carboxylic proton peak verify the formation of soyamide ferulate from soyamide. Integration of the ^{1}H-NMR spectrum (in DMSO-d_6) at 100 °C showed that the ratio of protons –N–CH_2–CH_2–O–CO to protons Ph–OCH_3 was 1.26 (expected value 1.33) while the ratio of protons Ph–CH=CH–CO–O– to protons –N–CH$_2$–CH_2–O–CO was 0.49 (expected value 0.50). Soyamide ferulate synthesis was also confirmed by ^{13}C-NMR spectra of soyamide ferulate. The ferulic carboxylic acid carbon signal observed at δ 168 ppm [14, 15] shifted to δ 166 ppm in the ^{13}C-NMR spectrum of soyamide ferulate. The methylene carbon of –N–CH$_2$–CH$_2$–O–CO– was observed at δ 61.33–61.07 ppm in soyamide ferulate and at δ 59.28–59.06 ppm in soyamide, exhibiting the expected shift to high field in soyamide ferulate.

Figure 4 combines GPC data for ferulic acid and soyamide ferulate. Ferulic acid eluted through the GPC column at 19.35 min corresponding to a molecular weight of 188 (theoretical molecular weight 194). Soyamide ferulate eluted at 17.92 min corresponding to a molecular weight of 636 (expected molecular weight 591 based on OH value of soyamide). The flow marker eluted at 21.73 min. Thus, the GPC data also validates the synthesis of soyamide ferulate.

It can be argued that the soyamide ferulate reaction has the potential to produce feruloyl oligomers and polyferulates as byproducts. However, the high reaction yield suggests that significant amounts of water-soluble feruloyl oligomers were not formed. A control reaction was conducted in the absence of soyamide to check for polyferulates. While ferulic acid is soluble in toluene in the presence of soyamide, ferulic acid was insoluble by itself even in boiling toluene, and continuous refluxing yielded a char. The ^{13}C-spectrum of soyamide ferulate did not exhibit a shift in the carbon signal at δ 147.93 ppm (phenolic carbon) confirming the absence of detectable amounts of polyferulate. The higher reactivity of soyamide's primary alcohol group relative to the phenolic hydroxyl group is likely to limit polyferulate formation.

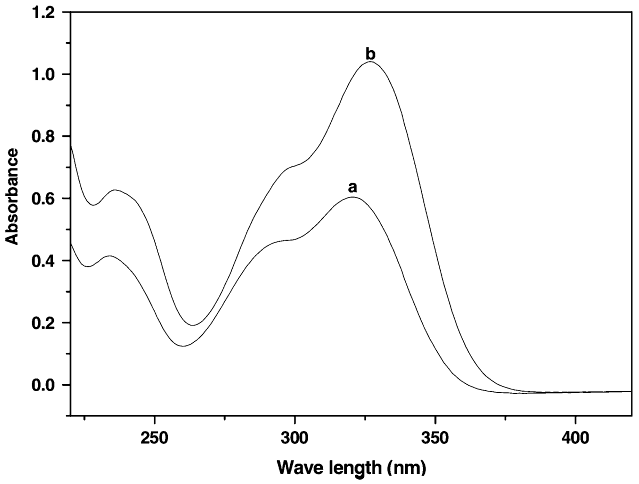


Fig. 6 UV–vis absorption spectra of *a* ferulic acid (3.29×10^{-5} M) and *b* soyamide ferulate (5.28×10^{-5} M)

UV–Visible Spectroscopy

UV–vis absorption spectra of ferulic acid and soyamide ferulate are displayed in Fig. 6. Pan et al. [16] studied the UV–vis absorption spectroscopy of ferulic acid and ethyl ferulate in 50% aqueous 2-methoxy ethanol and observed a red shift from 310 to 325 nm. Ferulic acid is characterized by $\lambda_{\max}$ at 320 nm while soyamide based ferulate exhibits $\lambda_{\max}$ at 327 nm corresponding to a molar extinction coefficient of 19,705 L mol^{-1} cm^{-1}. The 7-nm bathochromic shift arises as a result of soyamide esterification of ferulic acid. Since etherification on the phenolic hydroxyl group hardly affects the UV absorption spectra of ferulic acid, the bathochromic shift also supports the formation of soyamide based ferulate.

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