Cellulose functionalization with methyl ferulate in a switchable solvent system

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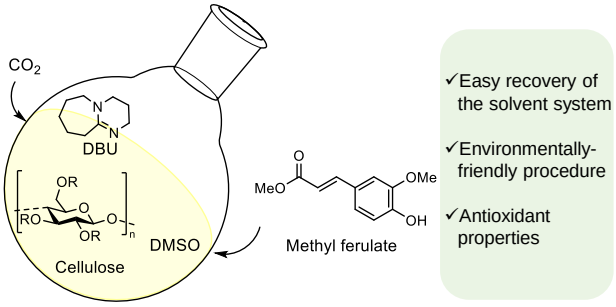


Abstract

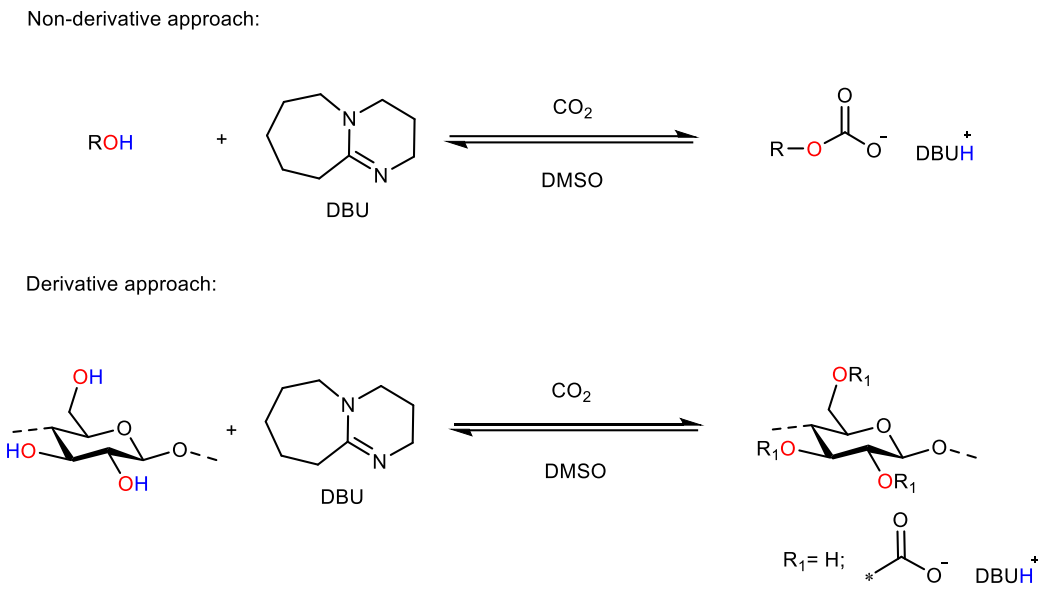
A direct transesterification of cellulose with methyl ferulate was achieved in a switchable ionic liquid solvent system, a particular class of ionic liquids that can change its polarity from non-ionic to ionic. An optimization of the reaction parameters was conducted and the extent of the transesterification was monitored via FT-IR spectroscopy as well as ^{1}H-NMR spectroscopy.

Subsequently, a series of cellulose esters with variable degrees of substitution (DS) was synthesized. Modifications of the derivatizing agent were also performed in order to evaluate the influence of functional groups on its reactivity, obtaining a maximum DS of 0.62. The thermal stability of the obtained cellulose ferulates was investigated, as well as their UV-absorption and antioxidant properties, revealing a free radical scavenging ability up to 78% in 120 minutes. Furthermore, the recyclability of the switchable solvent system was investigated, and recycling ratios up to 91% were obtained.

Introduction

In today's world, renewable resources and environmental sustainability are key factors in the pursuit of independence from fossil resources. Biopolymers, and polysaccharides in particular, have been the focus of much research in recent years due to their abundance and versatility. Materials like starch, chitin and chitosan, or cellulose offer a broad range of possible modifications and applications. Cellulose, in particular, has gained attention for its interesting properties, such as biodegradability, biocompatibility and low cost, as well as high thermal stability and mechanical resistance. This biopolymer is usually modified by grafting moieties onto the macromolecular chains to improve either its processability (pristine cellulose is not thermoformable/processable due to the absence of a glass transition temperature T_g and a melting temperature T_m)[1] or its mechanical properties. Heterogeneous modification of cellulose is widely applied in industry, however, this method has its drawbacks: in the *Acetic Acid Process* for example, for the production of cellulose acetate, over-stoichiometric amounts of reactant are necessary and the degree of substitution (DS) cannot be directly controlled, leading to a large amount of waste.[2] Cellulose is insoluble in common organic solvents due to the strong intra- and intermolecular hydrogen bonds

between the chains,[3] thus impeding conventional homogeneous modifications. A particular class of solvents capable of dissolving cellulose are Ionic Liquids (ILs), as they are capable of interrupting these hydrogen bonds.[2] Among the advantages of these solvents, such as low vapor pressure, a melting point below 100 °C, and recyclability,[4] problems related to their toxicity and harmfulness need to be considered.[5] In this context, a new class of ionic liquids has arisen as a more sustainable replacement for traditional ILs: CO_2 switchable solvent systems, for the first time reported in 2005 with the work of Jessop et al.[6] The concept behind the switchable systems is the possibility to "switch" a determined set of properties of a solvent: a non-ionic liquid can change its polarity into an ionic liquid upon the exposure to CO_2; simultaneously, the solvent can reverse back to its non-ionic state upon CO_2 removal.[6] Most commonly, an organobase (*e.g.* 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), or 1,1,3,3-tetramethylguanidine (TMG)) and an alcohol are present, together with dimethylsulfoxide (DMSO) as the solvent.[7] There are two possibilities to achieve a cellulose dissolution via a CO_2 switchable solvent system: non-derivative and derivative approaches. In the derivative approach, the OH-groups of cellulose react with CO_2 in the presence of a superbase, thus forming a soluble cellulose carbonate.[8] The non-derivative approach involves a simple alcohol (*e.g.* methanol, hexanol, octanol) as additional source of hydroxyl groups, forming a carbonate anion with the protonated base as counterion, which can finally act as a solvent for cellulose. The two different pathways are presented in **Scheme 1**. Recent studies have shown that in derivatization reactions applying this solvent system, the superbase can have a dual role: both promoting the solubilization process and acting as the catalyst in the subsequent cellulose functionalization.[9,10]



Scheme 1 *- Non-derivative (top) and derivative (bottom) approach for cellulose dissolution in a switchable solvent system, readapted from [2].*

According to the fourth and the fifth principles of green chemistry, established in 1998 by Anastas and Warner,[11] chemical syntheses should be designed minimizing toxicity, and selecting greener solvents, whenever necessary. DMSO, compared to other solvents, such as dimethylacetamide (DMAc), it is considered a greener alternative due to its physico-chemical properties (*e.g.* low vapor pressure) and low toxicity.[12] Moreover, the herein used solvent system offers an easy recovery, which is beneficial from a sustainability point of view. The solubilization of cellulose *via* this switchable solvent system allows further modifications to produce cellulose esters[13], ethers[14], and other cellulose derivatives[15–17]. A homogeneous modification can overcome the previously mentioned difficulties of heterogeneous processes, and, at the same time, it is a valid sustainable alternative if a switchable solvent system is used, as for instance recently demonstrated for cellulose acetate.[18]

In this context, the esterification of cellulose was carried out utilizing *methyl 3-(4-hydroxy-3-methoxyphenyl)acrylate*, the methyl ester of ferulic acid. Ferulic acid belongs to the

hydroxycinnamic acids (HCAs), a class of compounds bearing a C_3-C_6 skeleton and an aromatic group, such as cinnamic acid, p-coumaric acid, or caffeic acid.[19] Ferulic acid is a naturally occurring phenolic acid, widely distributed in edible plants, ester-linked to polysaccharides in primary cell walls of cereals and grasses,[20] rapeseed cake,[21,22] and fruits.[23] Ferulic acid ensures cohesion between polysaccharides (*e.g.* cellulose and hemicellulose) and lignin,[23] acting as a cross-linker.[24] Besides being bio-derived, safe, and possessing low toxicity,[25] another interesting property is the high antioxidant activity. The main mechanism of phenolic antioxidants consists of two stages, the radical trapping stage and the radical stabilizing stage,[26] that produces a stable compound (radical termination). A study from 2006 has shown that the antioxidant mechanism of methyl ferulate proceeds via dimerization and subsequent construction of a dihydrobenzofuran ring as the main termination process.[26,27] The scheme of the radical scavenging mechanism for methyl ferulate is shown in **ESI** (Scheme S2).

These antioxidant properties of ferulate esters have gained attention due to their possible applications: bonding ferulic moieties to biopolymer matrixes can lead to a biopolymer with interesting antioxidant properties. The possible range of applications applies from food preservation in food packaging, as well as in the biomedical field as membranes for hemodialysis, solving the difficulties that derive from the imbalance of reactive oxygen species (ROS) and antioxidant defense mechanism.[28] Antioxidants are generally used to decrease oxidative stress: polyphenols, for example, exhibit antioxidant activity, therefore they are widely used in the field of food packaging.[29] Considering the range of application of antioxidants, it is important that the final compound is biocompatible and possesses low-biotoxicity.

Besides its characteristic antioxidant properties, this substrate contains a double bond, a Michael system, as well as an aromatic group and a phenolic hydroxyl group. The presence of these

interesting functional groups could pave the way to post-modifications and offers the possibility of cross-linking. In a study from 2018,[30] it was investigated how the presence of bulky substituents grafted to cellulose can positively influence mechanical properties and thermal properties, revealing that aromatic ester groups can increase the T_g of the final cellulose esters, hence increasing rigidity. It was also noted that in order to improve the mobility of the cellulose chains, substituents with soft segments located between the bulky moiety and the cellulose chain are superior to those with the soft segments located at the end of bulky groups directly attached to the cellulose chain.[30] Therefore, phenolic acids are usually good candidates to reach improved mechanical resistance and enhanced thermal properties. The presence of the aromatic group improves rigidity and contributes to flame retardant properties, moreover the hydrophobicity increases compared to unmodified cellulosic fibers.[23] Modification of cellulose with syringic acid, vanillic acid, and p-hydroxybenzoic acid was already shown to improve the toughness and the ductility of the obtained cellulose ester films, despite the low degree of functionalization (DS<0.25). This was ascribed to the density of grafted rigid phenolic structure and the presence of -OH from phenolic groups that contributes to the hydrogen bonding.[31]

In this work, cellulose was functionalized utilizing methyl ferulate (*methyl 3-(4-hydroxy-3-methoxyphenyl)acrylate)* as derivatizing agent in a switchable solvent system consisting of DMSO/DBU/CO_2. The functionalization of cellulose was subjected to optimization of reaction parameters, as well as modification of the derivatizing agent to investigate its reactivity. A series of cellulose esters were obtained, and their thermal properties, UV-absorption properties, as well as antioxidant properties, were investigated.

Experimental

Materials

Cellulose (microcrystalline, powder, Sigma-Aldrich) was vacuum dried at 100°C for 24 h before usage.

Dimethylsulfoxide (DMSO, extra dry over molecular sieve, Acros Organics), DMSO for spectroscopy Uvasol® (>99.8%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, >98%, Fluorochem), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, >98%, TCI Chemicals), methyl 3-(4-hydroxy-3-methoxyphenyl)acrylate (99.97%, BLD Pharm), 1,1-diphenyl-2-picrylhydrazyl free radical (DPPH, >97.0%, TCI Chemicals), CO_2 (99.995%, AirLiquide), dimethyl carbonate (anhydrous, >99%, Sigma-Aldrich), H_2 (99.99%, AirLiquide), Palladium on activated charcoal (10% Pd basis, Sigma-Aldrich), ethyl acetate (>99%, Fisher Chemical), ethanol (>99.8%, Fisher Chemicals) and propan-2-ol (>99.5%, Fisher Chemical) were used without further purification. Deuterated solvents (DMSO-d_6 and $CDCl_3$) were purchased from Eurisotop.

Instruments

Infrared spectroscopy (IR). Infrared spectra of the samples were recorded using a Bruker ALPHA attenuated total reflection (ATR) IR spectrometer in the range of ν=400-4000 cm^{-1} at ambient temperature with 24 scans per measurement.

Nuclear magnetic resonance spectroscopy (NMR). ^{1}H NMR spectra were recorded using a Bruker Ascend 400 MHz with 16-128 scans, depending on the sample, a delay time d_1 ranging from 1 to 5 seconds, at 298 K. The chemical shift was reported in parts per million (ppm) and referenced to characteristic signals of deuterated solvents, *e.g.* DMSO-d_6 at 2.50 ppm or chloroform-d_1 at 7.26 ppm. ^{13}C NMR spectra were recorded using a Bruker Ascend spectrometer at 101 MHz with 1024-

8192 scans depending on the sample, delay time d_1 of 1 s at 298 K. The chemical shift was reported in parts per million (ppm) and referenced to characteristic signals of deuterated solvents, *e.g.* DMSO-d_6 at 39.52 ppm or chloroform-d_1 at 77.16 ppm. The signal multiplicity arising from spin-spin coupling was abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sept = septet, m = multiplet, br = broad signal. Coupling constants *J* were reported in Hz. 2D-NMR methods were performed for structure analysis and signals assignment: ^{1}H,^{1}H-correlated spectroscopy (COSY), ^{1}H,^{13}C-heteronuclear single quantum coherence spectroscopy (HSQC), ^{1}H-^{13}C-heteronuclear multiple bond correlation spectroscopy (HMBC).

Gas chromatography coupled with mass spectrometry (GC-MS): GC-MS measurements were performed on a Varian 431 GC instrument with a capillary column *FactorFour VS-5 ms* (30 m × 0.25 mm × 0.25 mm) coupled with a *Varian 210* electron impact (EI) ion trap mass spectrometer. Scans were performed from 40 to 650 *m/z* at a rate of 1.0 scans per second. The oven temperature program was: initial temperature 95 °C, ramp at 15 °C min^{-1} to 220 °C, hold for 4 min, ramp at 15 °C min^{-1} to 300 °C, hold for 2 min. The injector transfer line temperature was set to 250 °C. Measurements were performed in split-split mode (split ratio 50:1) using He as carrier gas with a flow rate of 1.0 mL min^{-1}.

Thermogravimetric analysis (TGA): Thermogravimetric measurements were performed using a TGA Q5500 from TA Instruments. The samples were dried under vacuum at 70 °C overnight before measuring. The samples (about 6 mg) were heated in a Pt crucible from 25 to 600 °C under nitrogen atmosphere at a heating rate of 10 °C/min. After the measurements, the weight loss was calculated in order to determine the degradation temperature ($T_{d,5\%}$ and $T_{d,\ 50\%}$) of the samples. $T_{d,5\%}$ is the temperature, at which 5% weight loss of the sample occurred, while $T_{d,50\%}$ is defined as the temperature at which 50% of the weight loss of the sample occurred. The onset temperature

(T_{Onset}) is the temperature extrapolated at the intersection point of inflectional tangents to the degradation curve.

Differential scanning calorimetry (DSC): DSC measurements were performed on a Mettler Toledo DSC 3 STARe system. 40 µL aluminum crucibles were used to weigh a precise amount of each sample, between 3 and 7 mg. The samples were measured in two heating cycles to delete the thermal history: from 25 to 200 °C, 200 to -50 °C, and -50 to 200 °C. DSC curves presented are relative to the second heating cycle. A heating or cooling rate of 10 K min^{-1} was applied.

UV-vis measurements: UV-vis spectra were obtained on a UV-vis spectrophotometer (Cary 3500 Multicell, Agilent Technologies) with 1 mL quartz cuvettes (pathlength 10 mm). Depending on the experiments, single absorbance values were recorded at 517 nm and spectra were recorded in the range of 190-800 nm.

General procedure for the synthesis of cellulose ferulates

Microcrystalline cellulose (MCC, 0.5 g, 3.08 mmol, dried) was weighed in a round bottom flask. DMSO (10 mL) and DBU (1.4 mL, 9.25 mmol, 3 eq. per anhydroglucose unit, AGU) were added and the mixture was stirred for 30 min at 40 °C while applying CO_2 (1 atm, balloon). After the cellulose dissolution, the reaction mixture was heated to 100 °C and the functionalization agent was added (3-6 eq. per AGU), the reaction was then stirred for 24-48 h depending on the sample. After the reaction, the mixture was cooled to room temperature, then precipitated in *i*PrOH to remove the unreacted reagent, solvents and DBU. The precipitate was filtrated and washed again with fresh *i*PrOH. For further purification, soluble samples were dissolved in DMSO and reprecipitated in *i*PrOH. Insoluble samples were washed with several aliquots of *i*PrOH. An

additional washing step with 0.5 M HCl was performed, if necessary, in order to remove DBU impurities. The filtrated product was dried under vacuum at 80 °C.

Synthesis of methyl 3-(3,4-dimethoxy phenyl) acrylate

Methyl 3-(4-hydroxy-3-methoxyphenyl)acrylate (methyl ferulate, 8 g, 0.038 mol), dimethyl carbonate (DMC, anhydrous, 12.9 mL, 0.154 mol, 4 eq.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.7 mL, 0.038 mol, 1 eq.) were mixed in a round bottom flask. DMSO (30.0 mL) was added as a cosolvent. The reaction mixture was stirred for 24 h at 90 °C. The crude product was diluted with ethyl acetate, then washed with 2 M HCl (2×), distilled water, and brine. The aqueous phase was extracted once more with ethyl acetate, the combined organic phases were dried over magnesium sulfate. The solvent was evaporated under reduced pressure, yielding the alkylated product as a yellow solid (8.41 g, quantitative). Complete characterization is shown in the **ESI** (Fig. S1-S3).

DS calculation for samples functionalized with methyl 3-(3-methoxy-4-hydroxy phenyl) acrylate (methyl ferulate)

The DS of the samples was determined using ^{1}H-NMR, taking into account the integrals of the distinctive signals from the double bond and aromatic protons of the ferulate moieties (6.25-8.00 ppm), as well as the AGU protons (consisting of five -C**H** and the two -C**H₂** protons) and the -OMe signal (2.75-5.50 ppm). By normalizing the integral of the double bond and aromatic protons to 5, the integration ratio (I_{ratio}) was calculated as follows, depending on the DS:

$$I_{\text{ratio}} = \frac{\text{Aromatic and double bond protons}}{\text{AGU protons and} - \text{OMe protons}} = \frac{5 * DS}{7 + 3 * DS} \qquad \text{Eq. 1}$$

Obtaining the DS from Eq. 1:

$$DS = \frac{7 * I_{ratio}}{5 - 3 * I_{ratio}} \quad \text{Eq. 2}$$

DS calculation for samples functionalized with methyl 3-(3,4-dimethoxy phenyl) acrylate (methylated methyl ferulate)

In this case, an adjustment of Eq. 2 was necessary to obtain the DS via ^{1}H-NMR, considering both the -OMe signals of the modified reagent. The I_{ratio} was calculated as:

$$I_{\text{ratio}} = \frac{\text{Aromatic and double bond protons}}{\text{AGU protons and} - \text{OMe protons}} = \frac{5 * DS}{7 + 6 * DS} \quad \text{Eq. 3}$$

And the respective DS equation is accordingly:

$$DS = \frac{7 * I_{ratio}}{5 - 6 * I_{ratio}} \quad \text{Eq. 4}$$

Evaluation of antioxidant properties via DPPH radical assay

Antioxidant properties of the samples were measured spectrophotometrically, *via* the literature known *2,2-diphenyl-1-picrylhydrazyl* (DPPH) radical assay.[32,33] Cellulose ferulate (**CF**) solutions were prepared in DMSO, at different concentrations. A fresh solution of DPPH (0.1 mM) in EtOH was prepared immediately before the measurements and kept dark (covered with aluminum foil). A fixed volume (125 µL) of **CF** solutions at different concentrations was added to 1 mL of the DPPH solution in EtOH, vortexed for 30 seconds, and the absorbance was measured at 517 nm (Abs_{sample}). The absorbance value was recorded and used to determine the DPPH Scavenging activity of the samples, according to Equation 5.[34]

$$\text{DPPH Scavenging Activity (\%)} = 1 - \frac{\text{Abs}_{\text{sample}} - \text{Abs}_{\text{blank}}}{\text{Abs}_{\text{control}}} * 100\% \qquad \text{Eq.5}$$

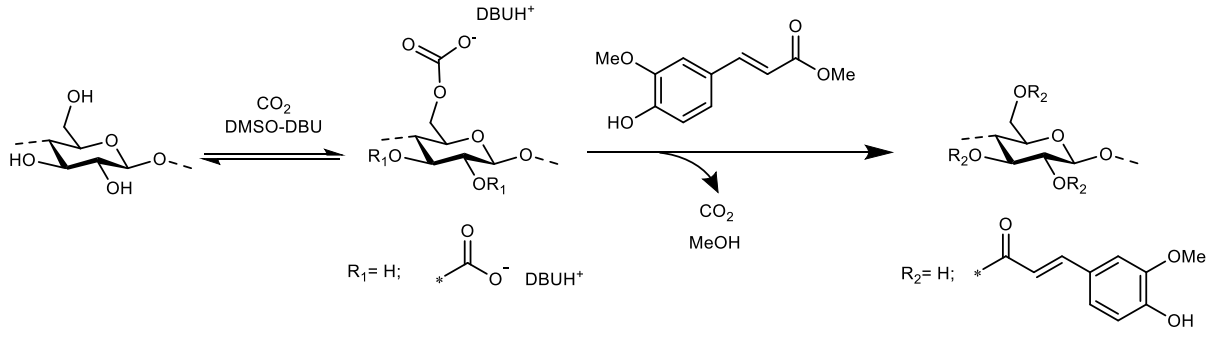
Where Abs_{sample} is the absorbance of the sample solutions at 517 nm, Abs_{blank} is the absorbance of the blank solution (125 μL of CF solution in 1 mL of ethanol, without DPPH). $Abs_{control}$ is the absorbance of the control solution (125 μL of DMSO in 1 mL of DPPH solution in ethanol). The absorbance values for the three sets of samples were recorded at different time intervals, and the plots of the free radical scavenging activity versus time were obtained.

General procedure for the recycling process

After filtration, the solids were dried under vacuum and the *i*PrOH was captured in a cooling trap. The mixture of DMSO, *i*PrOH, DBU, and non-reacted reagent that remained after filtration was distilled via fractional distillation. The first fraction, containing only iPrOH, was distilled at 60 mbar and 45 °C, and combined with the *i*PrOH from the cold trap. The second fraction, consisting of a mixture of *i*PrOH and DMSO, was collected at 25 mbar and 90 °C. Lastly, DMSO was distilled at 15 mbar and 100-110 °C. The remaining mixture after distillation, composed of unreacted reagent and DBU, was diluted with ethyl acetate and washed with 0.5 M HCl (2x) to protonate the DBU; the unreacted reagent was extracted in the organic phase. Afterwards, 6 M NaOH was added and DBU was extracted with ethyl acetate. The organic phases were dried over anhydrous $MgSO_4$, filtered and ethyl acetate was evaporated under reduced pressure. Purification of the extracted DBU was performed by distillation. Recycling Ratios (R.R.) were calculated from the ratio between used and recovered substance. Characterization of recovered solvents and calculation of the mixed fraction can be found in **ESI** (Fig. S14-S20).

Results and discussion

The investigated reaction to functionalize cellulose with methyl ferulate is shown in **Scheme 2**. At first, cellulose was solubilized by the formation of cellulose carbonate anions, with protonated DBU as the counterion. This compound is soluble in DMSO, allowing the shown esterification in a homogeneous solution.



Scheme 2 *- General reaction scheme of cellulose functionalization with methyl ferulate in a switchable solvent system.*

In a first attempt, a series of cellulose ferulates were synthesized to evaluate the optimal reaction conditions. In **Table 1 (Samples CMF 1-9)**, the investigated reaction parameters (temperature, time, cellulose concentration, and ester equivalents) are presented.

In **Fig.1**, the IR spectrum of unmodified cellulose and a typical spectrum of cellulose ferulate are presented. After transesterification, the characteristic bands of the C=O stretching vibration at 1692 cm^{-1}, C=C double bond stretching vibration (1629 cm^{-1}), and C_{Ar}=C_{Ar} of aromatic group stretching vibration (1592, 1514 cm^{-1}) are clearly visible in the spectrum.

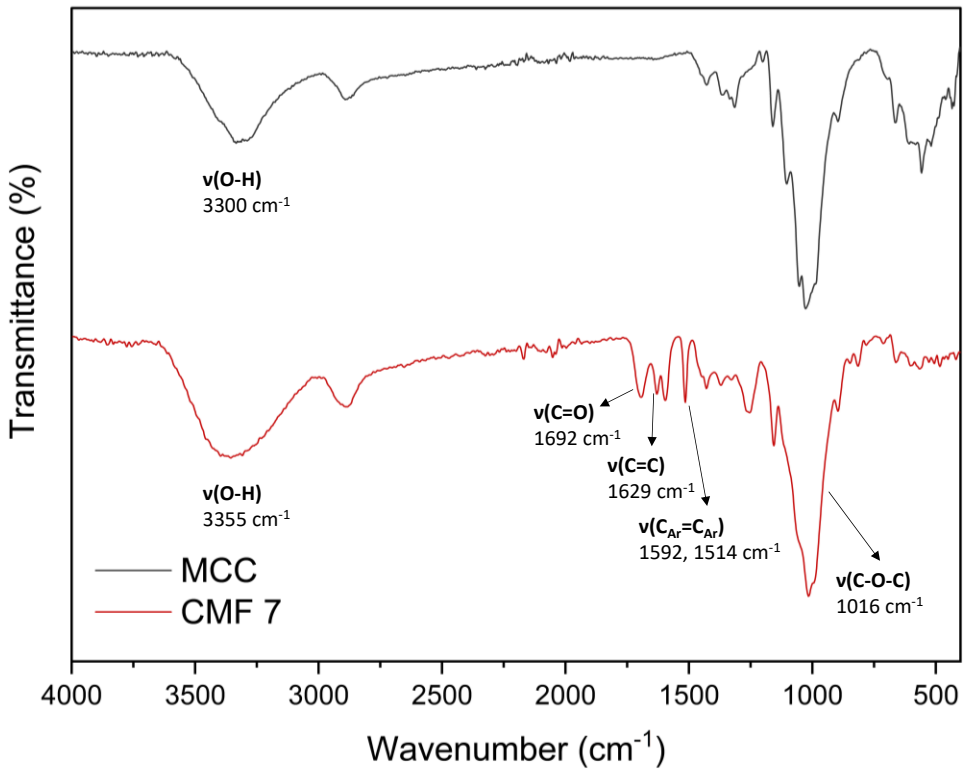


Figure 1 - *IR spectrum for MCC (unmodified) and sample CMF 7 (DS=0.27, see **Table 1**).*

The cellulose concentration was initially kept constant at 3.3 wt% to not increase the viscosity of the reaction mixture. Two sets of reaction temperatures, 70 and 100 °C, were tested and three different reaction times were evaluated. The set of samples obtained from the synthesis conducted at 70 °C was insoluble in DMSO, therefore it was not possible to analyze the samples *via* NMR. The extent of esterification was monitored via IR spectroscopy (**Fig.2**) by considering the intensities of the absorbance bands that confirm the ester bond formation, *i.e*. the carbonyl stretching band (C=O, 1692 cm^{-1}), the ferulate double bond stretching band (C=C, 1629 cm^{-1}) and the aromatic double bonds stretching bands (C_{Ar}=C_{Ar}, 1592, 1514 cm^{-1}). All IR spectra were normalized to the C-O stretching absorption band of the glucopyranose of cellulose (1050-1020 cm^{-1}), which is assumed to not be affected during the modification.

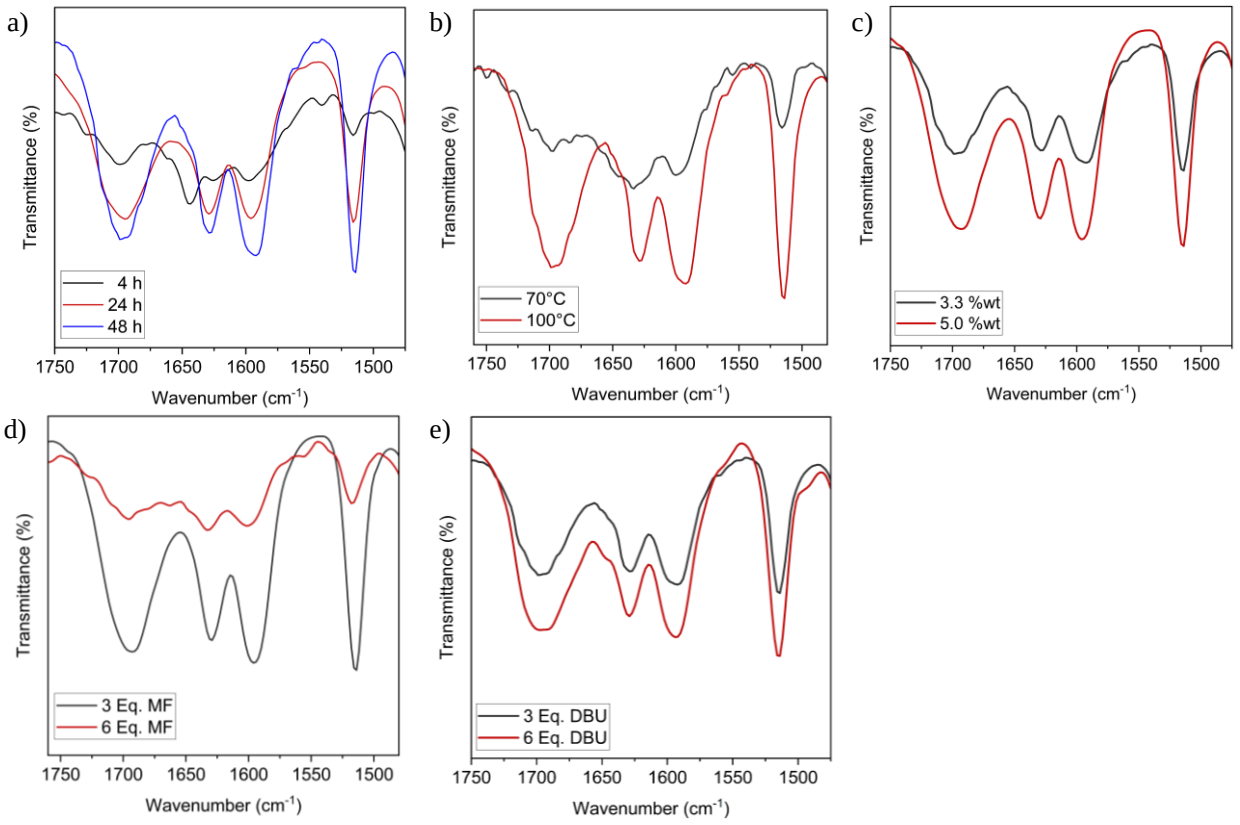


Figure 2 *- Intensity of the carbonyl stretching band in normalized IR spectra and the influence of different reaction parameters.*

First, the reaction time was evaluated. As the corresponding IR spectra show, the conversion is minimal after 4 h, but increases with time. The highest C=O absorbance intensity was found after 48 h (**Fig.2, a**). Hence, all subsequent syntheses were conducted for 48 h. Even if this specific solvent system showed less cellulose degradation during cellulose acetylation (in comparison to the heterogeneous system) thus confirming the milder conditions,[18] it is known that prolonged reaction times can cause degradation of the cellulose backbone,[35] therefore longer reaction times were not tested. A higher C=O signal intensity was found for the synthesis at 100 °C (**Fig.2, b**), if compared to 70 °C, while maintaining all other reaction parameters. Increasing the concentration of cellulose from 3.3 to 5.0 wt% further improved the conversion (**Fig.2, c**), as expected for a more

concentrated solution. According to previous works,[35,36] it is not convenient to increase the concentration of cellulose above 5.0 wt%, as the reaction mixture becomes too viscous, thus lowering the conversion. In addition, equivalents of derivatizing agents were varied, as usually an increase of reagent equivalents is generally associated with higher DS. In this regard, 3 and 6 equivalents per AGU were tested at 100 °C for 48 hours and 5.0 wt% cellulose concentration. The results show clearly that increasing the equivalents of reagent, in this case, did not improve the DS (**Fig. 2, d**). This can be explained by the acidic phenolic OH group of methyl ferulate, interfering with DBU, which will be discussed later. Increasing the amount of DBU only had a minor effect on the conversion (**Fig. 2, e**). After evaluation and optimization of the reaction parameters, the best reaction conditions for modification of cellulose with methyl ferulate were 100 °C, 48 hours, 5.0 wt% of cellulose, and 3 Eq. of reactant. With these conditions, a DS of 0.27 was obtained. The DS of cellulose can range from 0 (none of the hydroxyl groups is substituted) to a maximum of 3 (all hydroxyl groups of cellulose have reacted).

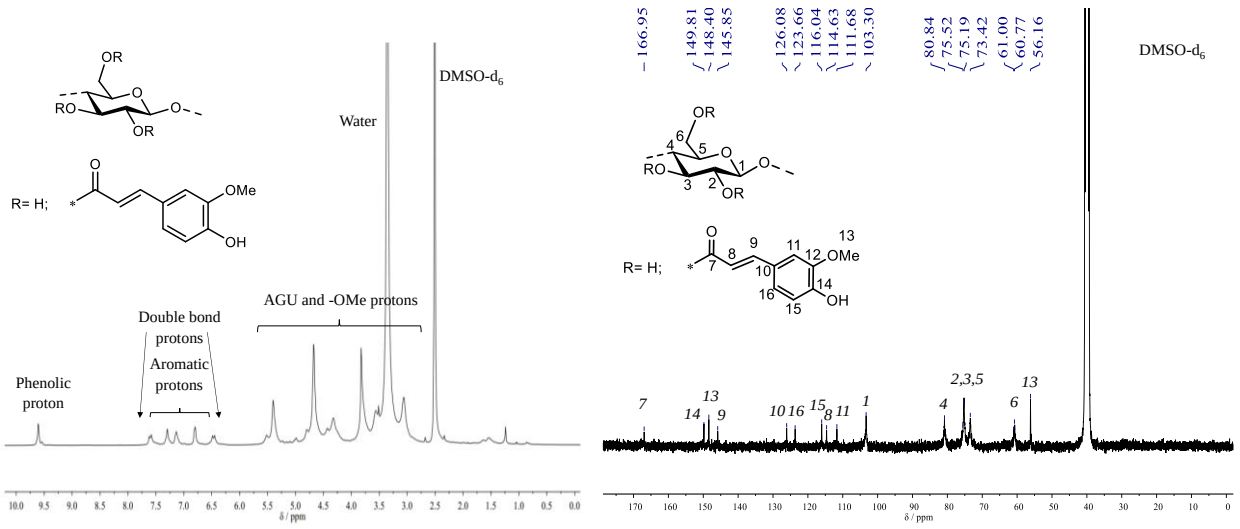


Figure 3 – left: ^{1}H-NMR spectrum of cellulose ferulate (CMF 9) in DMSO-d$_6$, right: ^{13}C-NMR spectrum of cellulose ferulate (CMF 9) in DMSO-d$_6$.

As a typical example, the ^{1}H-NMR spectrum of cellulose ferulate in DMSO-d_6 of sample (**CMF 9,** Table 1) is shown in **Fig. 3, left**. The AGU protons and the -OMe proton signals are observed as multiple broad, not precisely assignable signals at a chemical shift between 2.82 and 5.76 ppm, overlapping with the water signal. The peaks between 6.28 and 7.80 ppm are attributed to the protons of the aromatic structure and the double bond. The phenolic proton is observed at 9.60 ppm. Additional characterization of the sample was performed *via* ^{13}C-NMR, as depicted in **Fig.3**, **right**. Although the carbon spectrum is not well-resolved, it was possible to assign the signals by combining information from the literature[24,37] and an HSQC experiment (**ESI**, Fig S12). The carbonyl signal at 166 ppm indicates the linkage to the cellulose backbone. For instance, the carbonyl signal at 166 ppm indicates the successful modification to the cellulose backbone, but the determination of the preferred position of the ferulate linkages was not feasible, although a higher reactivity at C6 compared to the other positions was described before.[38,39] The DS values obtained with this derivatizing agent were comparably low (Table 1), indicating a low reactivity of the substrate. Methyl ferulate contains an aromatic hydroxyl group, which can interfere with the role of the DBU during the reaction, decreasing its catalytic activity and forming a salt, that requires further purification to yield the final product (*e.g.* HCl washing). Moreover, the derivatizing agent is a highly conjugated system, bearing electron-donating methoxy and hydroxy groups. This contributes to a lower carbonyl electrophilicity and thus probably to a lower reactivity towards cellulose. To the best of our knowledge, functionalization of cellulose with methyl ferulate in the DMSO/DBU/CO_2 switchable solvent system has not been investigated. Previous attempts to functionalize biopolymers with ferulic acid are present in literature, in different solvent systems. Earlier examples explored the esterification of cellulose using ferulic acid chlorides.[40–42] While these studies have shown promising results, it is essential to address the potential drawbacks

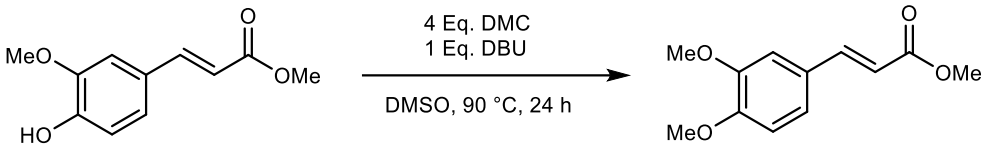
associated with these systems, such as the hazardous nature and toxicity of the reagent involved in the esterification process, which could pose challenges from both environmental and safety perspectives. In the work of Woranuch and Yoksan,[43] ferulic acid was grafted onto chitosan *via* a carbodiimide-mediated coupling reaction, reaching a DS of 0.37. Moreover, in a work from 2016,[44] starch was functionalized with ferulic acid *via* CDI (*N*,*N*´-carbonyldiimidazole) activation of the reagent, reaching a maximum DS of 0.35. Functionalization of cellulose with ferulic acid was performed in a homogeneous synthesis in DMAc/LiCl *via* dicyclohexylcarbodiimide (DCC) and *N*,*N*-dimethylaminopyridine (DMAP),[28] the DS obtained was of 0.56. The used activated acid derivatives, generated *in situ* using typical peptide coupling chemistry, are environmentally problematic due to generation of large amounts of waste and the toxicity of the used reagents. Additionally, noteworthy research works obtained cellulose ferulates via nucleophilic substitution after installing a leaving group on cellulose.[24,45] Moreover, also the literature-found DS are low and this further indicates a low reactivity of the substrate. To ensure that no side reactions between DBU and methyl ferulate occurred during the modification reactions, a reaction in absence of cellulose was performed. 1 Eq. of methyl ferulate and 1 eq. of DBU were mixed in DMSO-d_6 at 100 °C for 48 h and monitored via ^{1}H NMR spectroscopy. No side reaction was detectable, besides a shift of the DBU proton signals and a shift of the ferulate aromatic signals due to protonation (**ESI** Fig. S13).[46] As discussed before, doubling the equivalents of DBU from 3 to 6 per AGU increased the DS (**Fig.2, e**). This result further indicates a possible protonation of DBU by the phenolic hydroxyl group of methyl ferulate, which lowers the effective amount of DBU available for the reaction.

Table 1 *- Reaction parameters of cellulose ferulates syntheses; MF: methyl ferulate, MMF: methylated methyl ferulate.*

Sample	Temperature (°C)	Reaction time (h)	DBU (Eq.)	Reagent	Reagent (Eq.)	Cellulose Concentration (wt%)	DS
CMF 1	70	4	3	MF	3	3.3	-[a]
CMF 2	70	24	3	MF	3	3.3	-[a]
CMF 3	70	48	3	MF	3	3.3	-[a]
CMF 4	100	4	3	MF	3	3.3	-[a]
CMF 5	100	24	3	MF	3	3.3	-[a]
CMF 6	100	48	3	MF	3	3.3	0.13
CMF 7	100	48	3	MF	3	5	0.27
CMF 8	100	48	3	MF	6	5	-[a]
CMF 9	100	48	6	MF	3	3.3	0.29
CMMF 1	100	6	3	MMF	3	5	-[a]
CMMF 2	100	24	3	MMF	3	5	0.54
CMMF 3	100	48	3	MMF	3	5	0.47
CMMF4	100	24	3	MMF	6	5	0.62
CMMF 5	120	24	3	MMF	3	5	0.55

[a]Not determined due to insolubility.

In order to overcome this problem, the phenolic group of methyl ferulate was methylated. A facile synthesis method was modified and adapted from the literature,[47] utilizing dimethyl carbonate (DMC), DBU, and DMSO, as presented in **Scheme 3**. The synthesis yielded *methyl (E)-3-(3,4-dimethoxyphenyl)prop-2-enoate* (methylated methyl ferulate, MMF) quantitatively, and this substrate was then used for the functionalization of cellulose.



Scheme 3 *- Reaction scheme of the methylation of methyl ferulate.*

The reactivity of the methylated derivatizing agent was tested, alongside an optimization of reaction parameters. The temperature and the cellulose concentration were kept at 100 °C and 5 wt%, respectively, as these conditions showed the highest observed DS, when MF was used as the reactant. First, the reaction time was investigated. Three different reaction times were tested, 6, 24, and 48 h (samples **CMMF 1-3** in **Table 1**, respectively). The DS increased in time and after 24 h a DS of 0.54 was obtained. After 48 h of reaction a slight decrease of the DS to 0.47 was observed, therefore, the best reaction time was set to 24 h. The observed results could be confirmed by IR spectroscopy (**ESI**, Fig. S11).

The influence of the derivatizing agent equivalents were tested also for MMF, revealing that doubling the equivalents of MMF led to a slight increase in the DS from 0.54 to 0.62. Increasing

the temperature from 100 to 120 °C (**CMMF 3** vs. **CMMF 5**, **Table 1**) did not increase the DS considerably.

Thermal properties of the obtained cellulose esters

In order to investigate the thermal properties of the modified celluloses, TGA measurements were performed on samples with high DS. In **Table 2**, the $T_{d,5\%}$ and $T_{d,50\%}$ are presented. The TGA curves are presented in the **ESI** (Fig. S21).

Table 2 *- Thermal properties of the obtained samples.*

Sample	$T_{d,5\%}$ **(°C)**	$T_{d,50\%}$ **(°C)**	**Onset Temperature (°C)**	**Reagent**	**DS**
MCC	338	369	344	None	-
CMF 7	281	362	287	MF	0.27
CMMF 4	273	355	311	MMF	0.62

All samples exhibit a major single step decomposition. Pristine cellulose shows the highest thermal stability with a $T_{d,5\%}$ of 338 °C. The derivatized celluloses showed a $T_{d,5\%}$ and $T_{d,onset}$ lower than the reference sample of microcrystalline cellulose. This is in agreement with results from Guo et al.,[29] where cellulose 3-(2-hydroxyphenyl) propionate esters displayed a lower degradation temperature with increasing DS values. No considerable differences were observed between **CMF 7** and **CMMF 4**. The samples are stable up to 200 °C, which confirms the satisfactory thermal stability of the modified cellulose. DSC measurements were also performed on the samples to

investigate the effect of introducing ferulate moieties on the glass transition temperature (T_g). Despite the low DS observed in the samples, the introduction of ferulate moieties led to the presence of a discernible T_g (**ESI**, Fig. S22). This can be attributed to the bulky nature of the ferulate groups, which disrupt the intermolecular hydrogen bonding network in cellulose. No significant differences in the T_g values among the various samples were observed. This may be attributed to the relatively small differences in the DS of the cellulose ferulate esters. A previous study[48] reported a decrease in T_g of cellulose benzoate by 31 °C when the DS varied from 0.73 to 2.73. These findings suggest that while the bulkiness of the ferulate moieties contributes to the presence of a T_g, the small differences in DS among our samples may not significantly affect the observed T_g values.

UV/Vis measurements

The UV/Vis absorption spectra of the samples **CMF 7** and **CMMF 4** are shown in **Fig. 4**. Strong absorption was observed in the UVA-UVC regions for cellulose ferulates, further indicating the successful functionalization of the cellulose. Additionally, methylating the reagent did not alter the UV/Vis absorption properties of the final cellulose esters significantly. The maximum absorbance was found at 331 nm in the UVA region, indicating possible use of the material as a UV-absorber. Ferulic acid and its derivatives are widely utilized in skincare formulations as photoprotective agents, delayer of skin photoaging, and brightening components.[25] This could open the way to a wide range of applications where UV-absorption is required, such as in the cosmetic field.

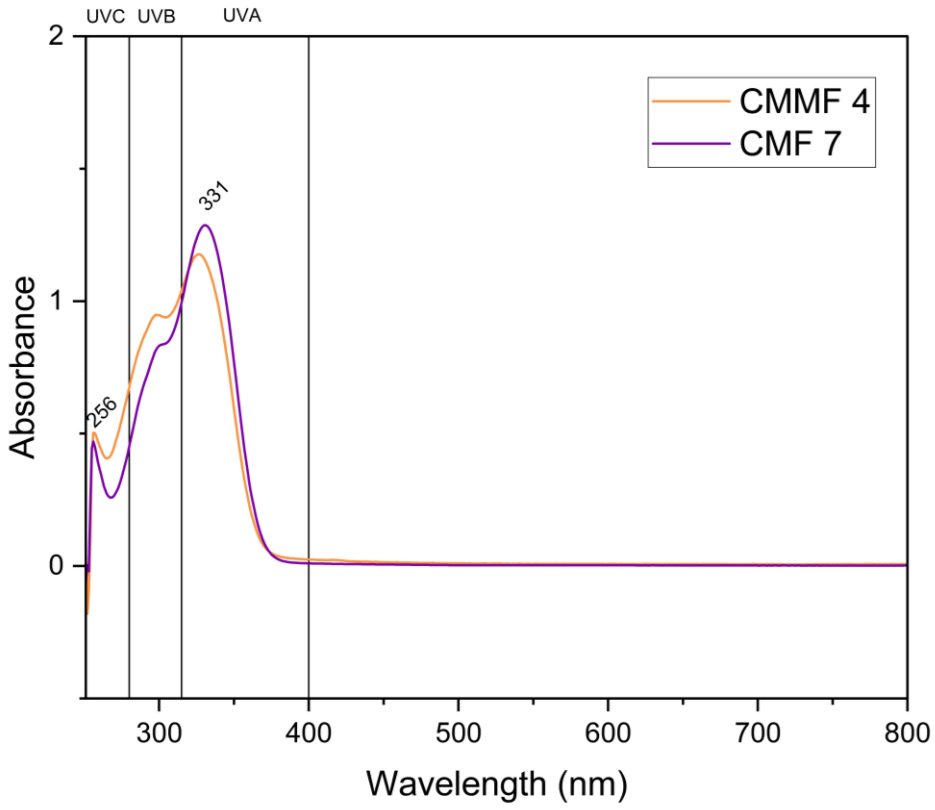


Figure 4 *- UV/Vis absorption spectra of samples CMF 7 (violet) and CMMF 4 (orange).*

Antioxidant properties

Antioxidant properties of the sample CMF 7 (DS: 0.27, cellulose functionalized with methyl ferulate) were measured spectrophotometrically, *via* the literature known *2,2-diphenyl-1-picrylhydrazyl* (DPPH) radical assay. This method is highly sensitive and the concentration of DPPH radicals can be followed by monitoring the absorbance peak of DPPH solutions at 517 nm.[49] This assay is based on the principle that a DPPH radical can accept a hydrogen atom from a scavenger molecule, the antioxidant, resulting in the reduction of DPPH· to $DPPH_2$. The initial purple color of DPPH thus changes upon reaction with the antioxidant to yellow with a concomitant decrease in the absorbance of the aforementioned absorption peak.[50,51] The reaction

between the DPPH radical and a generic antioxidant, AH, is depicted in Scheme S1 **(ESI)**. The absorbance values were recorded at different time intervals, and the results of the free radical scavenging activity versus time at 25 °C are shown in **Fig. 5a**.

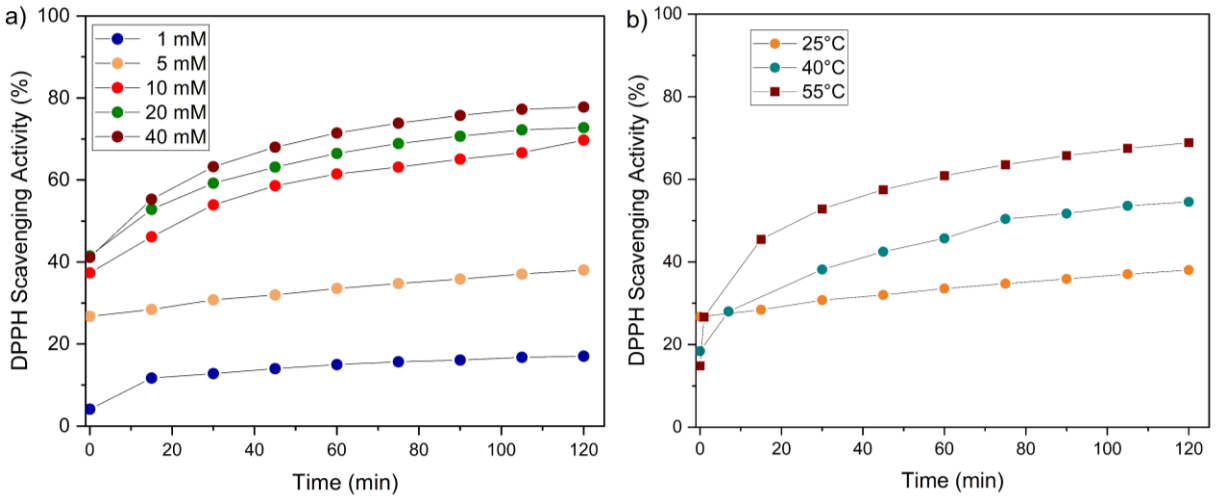


Figure 5 *- a: DPPH Scavenging Activity of CMF 7 at 25 °C, b: DPPH scavenging activity of the 5 mM sample (CMF 7) at different temperatures.*

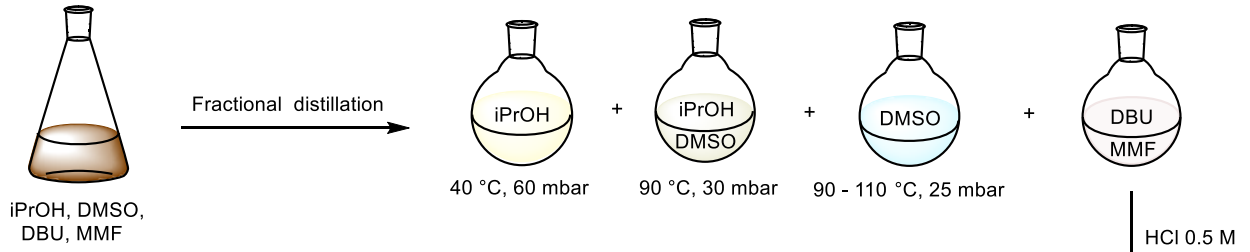
The samples were expected to show good antioxidant properties, since ferulic acid is known for its antioxidant features.[27] The absorbance values were recorded immediately after preparing the solutions. After 120 minutes at 25 °C, the free radical scavenging activity was assessed to be 17, 38, 70, 73 and 78%, for the solutions 1, 5, 10, 20, and 40 mM, respectively. The increase in CMF 7 concentration is associated with the yellowing of the samples (**ESI,** Figure S23), caused by the decrease of the absorbance at 517 nm due to reaction of DPPH with the ferulic acid moieties. Increasing the concentration from 10 to 40 mM did not lead to a significant increase in the free radical scavenging activity at the final time of the test. Recently, it has been reported that the free radical scavenging activities for cellulose-3-(2-hydroxyphenyl) propionate esters with a DS of 2.35 reached 100% DPPH scavenging activity after 30 minutes, at a concentration of 40 mM.[29] These

results are higher than the one obtained for CMF 7 at a concentration of 40 mM (78%), but the DS of CMF 7 (0.27) is significantly lower. The 5 mM solution of CMF 7 was also tested at different temperatures. The free radical scavenging activity increased with increasing temperature, reaching the values of 55 and 69% at 40 and 55 °C, respectively (**Fig.5b**). This is in accordance with reported literature data on scavenging activity and temperature dependance.[29,52] The antioxidant properties of CMF 7 were also compared with the antioxidant properties of CMMF 4, the cellulose ester functionalized with MMF (**ESI**, Figure S24-25), showing that antioxidant properties are lost when the hydroxyl group of methyl ferulate is substituted with a methoxy group, as expected, because of the loss of hydrogen atom donating capacity of the substrate.

Recycling tests

With the best reaction conditions found for CMMF 2 (**Table 1**), a larger batch of cellulose ferulate was prepared, in order to maximize the accuracy of the recycling procedure. The first fraction collected by distillation was composed only of *i*PrOH, and also the *i*PrOH captured in the cold trap was added to the recovered fraction (**ESI**, Fig. S14-15). The second fraction collected presented a mixture of *i*PrOH and DMSO, and molar ratios were calculated from NMR data (**ESI**, Fig. S16, Table S1). This fraction can be reused in other precipitations as a small amount of DMSO (6%) is not affecting the solubility of cellulose ferulates considerably. The third fraction collected, at 25 mbar, contained recycled DMSO (**ESI**, Fig. S17-18). Finally, the DBU fraction was obtained after extraction and further purified by distillation (0.1 mbar, 150 °C, **ESI**, Fig S19-20). The scheme for the recycling procedure and the obtained Recycling Ratios (R.R.s) are shown in **Scheme 4**. High R.R.s were obtained for *i*PrOH and DMSO. The recovery yield of DBU is slightly lower than the reported literature data.[18,29] This might be explained by DBU losses during the extraction and the subsequent distillation. Nevertheless, the recyclability of the solvent system and the *i*PrOH used

for the precipitation was successful, yielding recovered solvents with high purity that could be further utilized in other syntheses.



Substance	Used [g]	Recovered [g]	Recycling ratio (R.R., %)
iPrOH	248.9	221.9+3.9*	91%
DMSO	44.7	33.5+0.3*	76%
DBU	5.9	3.7	62%

*: collected in the mixed fraction

Scheme 4 - Recycling scheme and recycling ratios (R.R.) for the recovered substances.

Conclusion

In this study, a series of cellulose ferulates were successfully synthesized using the switchable solvent system DMSO/DBU/CO_2. This system provided an efficient *in situ* catalytic dissolution and functionalization medium for cellulose under mild conditions. Cellulose esters were obtained via a transesterification reaction between cellulose and methyl ferulate (MF) and characterized via ^{1}H-NMR and IR spectroscopy. The influence of reaction temperature, time, cellulose concentration, and equivalents of derivatization agent were evaluated and led to a maximum DS of 0.27 for MF. By investigating MMF and performing model reactions, the influence of the phenolic hydroxyl group of MF was demonstrated. The thermal properties of the samples were analyzed by TGA measurements, revealing their satisfactory thermal stability. Antioxidant properties were evaluated via the DPPH radical assay, exhibiting up to 78% of radical scavenging activity for cellulose ferulates with a DS of 0.27 in a 40 mM solution. Overall, this study

demonstrates the successful synthesis of cellulose ferulates, using an efficient and mild *in situ* catalytic dissolution and functionalization medium, which could have potential applications in the fields of cosmetics and antioxidants.

Associated content

Supporting Informations. ^{1}H-NMR spectra of all soluble compounds, as well as IR peaks, calculations and characterization of the recycling fractions, TGA curves, DSC curves, antioxidant properties schemes and data, including photographs of the samples (PDF)

Ackowledgments

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