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COMMUNICATION

Gallic acid derivatives as stabilizers in cellulose solutions: analysis by ^{31}P NMR spectroscopy

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Abstract Lyocell dopes for cellulosic fiber manufacture, i.e., cellulose solutions in *N*-methylmorpholine-*N*-oxide monohydrate, are commonly stabilized by propyl gallate, or alternatively by recently proposed gallic acid amide derivatives. In this study, the analysis of the stabilizer and its major degradation products, ellagic acid and ellagoquinone, is investigated. The stabilizer-derived compounds are readily extracted from the dopes with polar aprotic solvents without solvent or cellulose interference. This is followed by the derivatization of the OH groups with a phosphitylation agent and subsequent ^{31}P NMR analysis—an approach frequently used to differentiate and quantify OH groups in lignins. The chemical shifts of the resulting phosphites are reported and structures of the stabilizer derivatives are discussed. The ^{31}P NMR approach offers a straightforward way to analyze the stabilizer chemistry in the Lyocell process.

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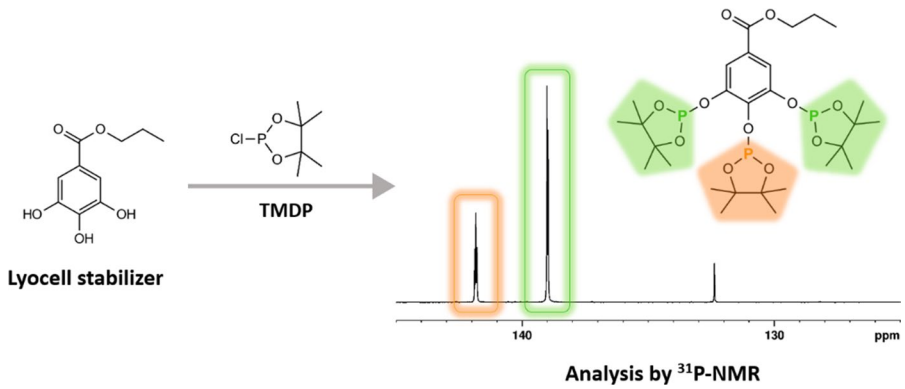
Graphical abstract



Keywords Antioxidants · Cellulose · Cellulosic fibers · Ellagic acid · Gallic acid · Lyocell process · *N*-methylmorpholine-*N*-oxide · NMMO · ^{31}P NMR spectroscopy · Stabilizer

Introduction

Propyl gallate (**2**), the *n*-propyl ester of gallic acid (**1**), is the classical stabilizer used for Lyocell dopes, i.e., solutions of cellulosic pulps in *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate, which are used for spinning of cellulosic fibers (Firgo et al. 1995; Fink et al. 2001). It exerts multiple actions, being effective by holding both homolytic (radical) and heterolytic (ionic) degradation processes at bay (Rosenau et al. 2005; 2002). The former class of side reactions is mainly induced by redox-active transition metal ions, while the latter primarily involves NMM-derived carbenium–iminium ions which trigger the autocatalytic, strongly exothermic degradation of NMMO (Rosenau et al. 1999). It also reduces the unwanted oxidation of cellulose (Ahn et al. 2019; Potthast et al. 2005) in the spinning dope which is the reason for chain degradation according to β-alkoxy elimination mechanisms in the prevailing alkaline medium (Öztürk et al. 2009; Hosoya et al. 2018).

Propyl gallate rather often accompanies NMMO in other uses of the *N*-oxide, such as chemical synthesis or biorefinery applications. In several of these cases, it is not necessarily required for chemical reasons (Albini 1993) but is simply used because the original combination of NMMO and stabilizer in Lyocell fiber production has become so common and widespread that it has been quasi "automatically" adopted for other areas of application. In analytical and synthesis applications of NMMO, the presence of propyl gallate or other gallic acid derivatives can be outright counterproductive: as a very good chain-breaking antioxidant it might interfere with the intended analytical purpose, such as radical trapping (Stolze et al. 2003), or with the synthesis target, such as oxidations or demethylation to be carried out (Rosenau et al. 2004; Yokota et al. 2008). In biorefinery applications, mostly aqueous solutions of "stabilized" NMMO are applied for biomass pretreatment (e.g., Aslanzadeh et al. 2014; Goshadrou et al. 2013; Shafiei et al. 2010; Taherzadeh and Karimi 2008; Wikandari et al. 2016) or activation purposes towards better saccharification (e.g., Cai et al. 2016; Khodaverdi et al. 2012; Kuo and Lee 2009; Liu et al. 2011; Poornejad et al. 2013), and in these cases the presence of propyl gallate usually goes unnoticed and is not further considered.

Besides propyl gallate (**2**) as the standard Lyocell stabilizer, gallic acid amides (amide **3** and

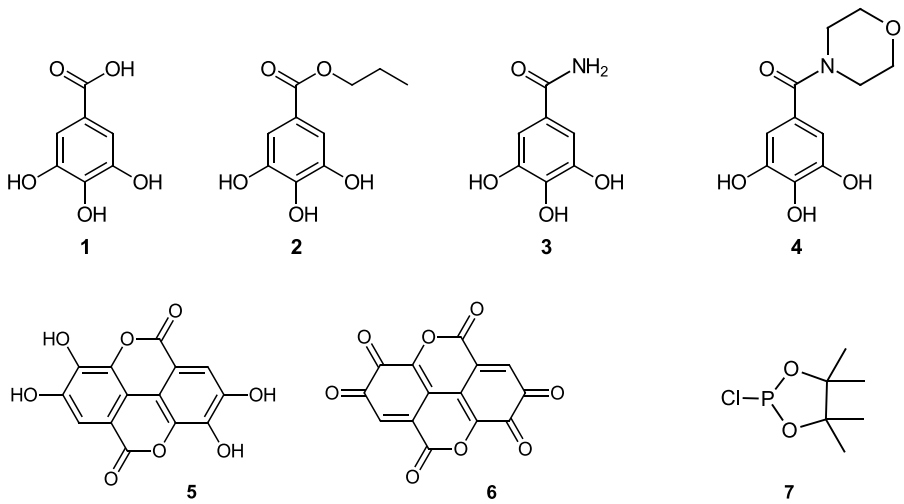


Fig. 1 Chemical structures of gallic acid (**1**), its ester and amide derivatives (**2–4**) used as Lyocell stabilizers and their main reaction products (**5**, **6**) as well as the derivatization agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, **7**) for qualitative and quantitative hydroxy group analysis by ^{31}P NMR

morpholide **4**) have recently gained attention because of lower discoloration of the dopes than with propyl gallate (Rosenau et al. 2005; 2007; Hettegger et al. 2022). The main reaction products of the stabilizers, no matter whether gallic esters or amide derivatives are used, are the hydrolysis product gallic acid (**1**), ellagic acid (**5**) as the product of radical coupling and entropically driven lactonization, and the ellagobis(*ortho*-quinone) (**6**) as the result of further oxidation (Fig. 1).

All these gallic acid derivatives have phenolic hydroxy groups as a common structural feature (Fig. 1). Their structural similarity to the phenolic units in lignin (e.g., Balakshin et al. 2015, 2020) is obvious. Moreover, gallic and ellagic acid are key constituents of gallotannins and ellagitannins, respectively (e.g., Bianco et al. 1998; Shalini et al. 2014), in which they are esterified with the OH groups of monomers of the same structure (depsides) and with those of glucopyranose units.

Hydroxy groups in natural lignins or technical lignins are commonly differentiated and quantified according to a ^{31}P NMR protocol which has been introduced by Argyropoulos (Argyropoulos et al. 1993; Argyropoulos 1994, 1995; Faix et al. 1994). The hydroxy groups, both aliphatic and aromatic ones, react with a chlorophospholane derivatization reagent (Granata and Argyropoulos 1995), mostly under catalysis with pyridine or in pyridine as the solvent, and are quantitatively converted into their corresponding phosphites, which is the prerequisite to hydroxy group quantitation. The OH functionalities of carboxylic acids are usually modified as well (Meng et al. 2019; Korntner et al. 2015b). The advantages of the method are its easiness and generality: the derivatization is mostly performed in situ in the NMR tube, and the interpretation of the spectra is straightforward due to the high sensitivity and the broad chemical shift range of the ^{31}P nucleus in NMR. The ^{31}P approach for hydroxy group quantification has become a standard tool in lignin chemistry (Saake et al. 1996; Crestini and Argyropoulos 1997; Argyropoulos and Zhang 1998; Tohmura and Argyropoulos 2001; Jiang and Argyropoulos 1998; Akim et al. 2001; Guerra et al. 2008; Zinovyev et al. 2018; Wurzer et al. 2021), but it has also been applied to other topics in wood and pulping chemistry, such as the analysis of polyhydroxyalkanoates or cellulose esters (Spyros et al. 1997; King et al. 2010), chemically or thermally modified wood (Fu et al. 2007; King et al. 2009; Sadeghifar et al. 2014), the monitoring of radical species during pulp bleaching (Argyropoulos et al. 2006) or the analysis of cellulosic key chromophores (Korntner et al. 2015a). It appeared somehow logical to apply the ^{31}P NMR method to the analysis of the Lyocell stabilizers and their reaction products, due to their structural similarity to lignin subunits. In this communication, we present the corresponding studies and report the respective ^{31}P NMR data of the phosphite derivatives of the Lyocell stabilizers and their main reaction products.

Materials and methods

All reagents and solvents were commercially available. They had a purity of > 99% and were used without further purification. Glassware was dried in a vacuum oven before use. The derivatization agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, **7**) was synthesized according to an in-house standard protocol.

The NMR spectra were recorded on a Bruker Avance II 400 spectrometer (^{1}H resonance at 400.13 MHz, ^{13}C resonance at 100.61 MHz, and ^{31}P resonance at 161.98 MHz) equipped with a 5 mm nitrogen-cooled cryo-probehead (Prodigy) with z-gradient at RT. Data processing was performed with the software Bruker Topspin 3.6.3. Chemical shifts were referenced to the solvent signals for $CDCl_3$: δ (^{1}H) = 7.26 ppm, δ (^{13}C) = 77.00 ppm, and C_5D_5N: δ (^{1}H) = 7.22, 7.58, 8.74 ppm, δ (^{13}C) = 123.87, 135.91, 150.35 ppm. To allow for an overall comparability of the results, pyridine (C_5H_5N) has been utilized for all NMR chemical shift calibrations, regardless of whether deuterated or non-deuterated pyridine was used for the measurements.

Derivatization of OH groups (phosphitylation) was carried out based on literature (Meng et al. 2019) and our previous work (Korntner et al. 2015b). In a dry vial, the samples (10 mg) were dissolved in dry, perdeuterated pyridine (600 µL) under shaking and the vessel was closed with a septum. The phosphitylation reagent **7** (50 µL) was added through the septum with a syringe to minimize any contact between reagents and moisture. The sample was shaken for 1 h at RT and transferred to an NMR tube. ^{31}P spectra were acquired with ^{1}H decoupling using a relaxation delay of $d1 = 1$ s, an acquisition time of 0.63 s and a 90° ^{31}P pulse set to 11.9 µs at a power level of 28 W. If quantitation is needed, 200 µL of a stock solution containing the internal standard *N*-hydroxy-5-norbornene-2,3-dicarboxylic acid imide (e-HNDI, 0.02 mmol mL^{-1}) is added, following a previously developed protocol (Korntner et al. 2015b). Derivatized e-HNDI gives a ^{31}P NMR resonance, downfield to the derivatized gallic acid derivatives, at 153.8 ppm.

Results and discussion

Lyocell solutions contain almost exclusively strongly hydrophilic substances, namely NMMO monohydrate and cellulose. The only hydrophobic—or better: less hydrophilic—compounds present in significant (percent) amounts are gallic acid derivatives used as stabilizers (gallic acid esters or amides), and their degradation products, mainly free gallic acid and ellagic acid. Gallic acid esters, gallic acid amides and ellagic acid can, in principle, be readily extracted from Lyocell dopes with polar aprotic solvents without interference from the solute cellulose or the solvent NMMO. This requires, however, a neutral or acidic medium. Since Lyocell solutions under industrial conditions contain up to 3% of *N*-methylmorpholine (NMM) and morpholine, the main products of NMMO degradation, their pH is around 10. At this pH, the phenolic gallate compounds are—at least partially—present in the corresponding phenolate salt form (with morpholinium and *N*-methylmorpholinium as countercations) and not extractable. Gallic acid, with a pK_a of 4.5, even requires a pH below 3 to be completely extracted from aqueous solutions. For extraction of the gallate compounds, the Lyocell solution must be diluted with water—for practical reasons as spinning dopes of cellulose in NMMO monohydrate are solid at RT—and acidified to convert phenolates and acids into the respective protonated forms.

In practice, the Lyocell dope was diluted 1:10 (v/v) with water and stirred with Dowex® acidic ion exchange resin (1 g/100 mL). The resin converts the salts into the free acid forms, but at the same time does not cause any ester or amide cleavage as tested with ester **2** and amide **3**. It is easily removed by filtration, along with precipitated cellulose, and can thus be used in a "traceless" way. Toluene was used as the organic extraction medium. It has very good solution properties for the gallic acid derivatives, and the extracts do not need to be dried in a separate step, because toluene is an efficient water entrainer. Evaporation of the toluene under reduced pressure thus azeotropically removes water as well and provides a dry analyte mixture of the gallic acid derivatives, which is ready to be dissolved in the derivatization medium for phosphitylation and subsequent NMR measurement. Pyridine-d_5, which dissolves all gallic acid derivatives efficiently, was the solvent of choice for this purpose: it acts as an effective derivatization medium, a

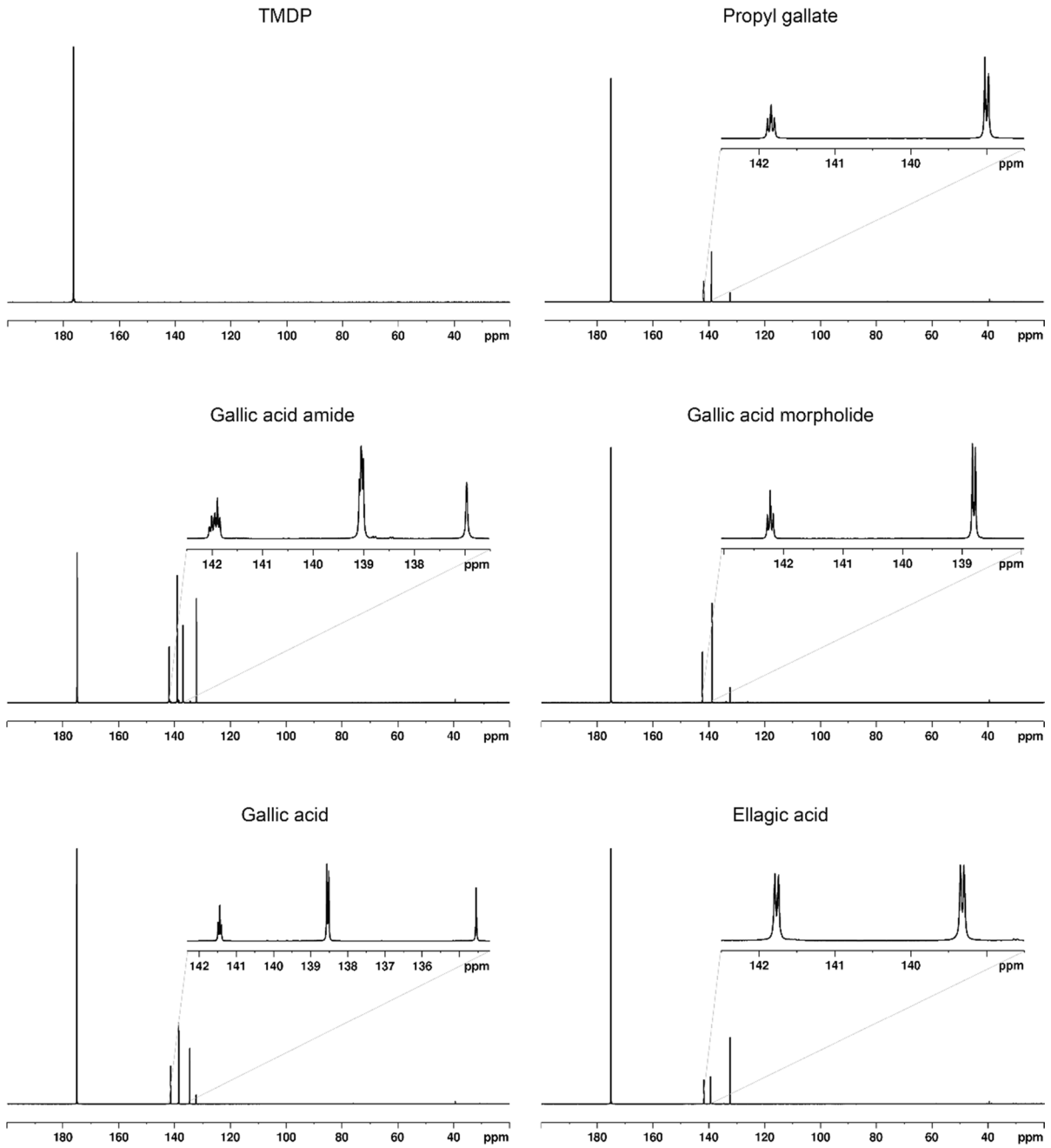


Fig. 2 Proton-decoupled ^{31}P NMR spectra of derivatization reagent TMDP **7** (upper left), the derivatized stabilizers propyl gallate **2** (upper right), gallic acid amide **3** (middle left) and gallic acid morpholide **4** (middle right), and the stabilizer degradation products gallic acid **1** (bottom left) and ellagic acid **5** (bottom right). Derivatization medium and NMR solvent: C_5D_5N (pyridine-d_5). The singlet at around 130 ppm comes from the minor hydrolysis byproduct of the phosphitylation reagent TMDP, carrying an OH group instead of the Cl

catalyst for the derivatization reaction, a trap for the generated HCl, and as an NMR solvent at the same time. The derivatization is therefore conveniently carried out in the NMR tube, using 10 mg of analyte. The evaporative removal of the extraction solvent toluene and the acidification with Dowex® resin was

Table 1 ^{31}P NMR shifts (^{1}H-decoupled, in ppm) of derivatization reagent TMDP (**7**), derivatized Lyocell stabilizers **1**–**4,** and stabilizer byproducts **5**–**6**

Compound	Chemical shift ^{31}P NMR [ppm][a]	Remark
Reagent **7**	176.3	
Derivatized **1**	138.5 [b](3,5–O–P, d, J = 8.0 Hz, 2P) 141.4 [b](4–O–P, t, J = 8.0 Hz, 1P)	COOH derivatization: see text
Derivatized **2**	139.0 [b](3,5–O–P, d, J = 8.0 Hz, 2P) 141.8 [b](4–O–P, t, J = 8.0 Hz, 1P)	
Derivatized **3** (gallamide)	139.1 [b](3,5–O–P, d, J = 8.0 Hz, 2P) 142.0 [b](4–O–P, t, J = 8.0 Hz, 1P)	NH-derivative: see Supplementary Material
Derivatized **4** (morpholide)	138.8 [b](3,5–O–P, d, J = 8.0 Hz, 2P) 142.2 [b](4–O–P, t, J = 8.0 Hz, 1P)	
Derivatized **5** (ellagic acid)	139.3 [b](3–O–P, d, J = 8.0 Hz, 1P) 141.8 [b](4–O–P, t, J = 8.0 Hz, 1P)	Centrosymmetric molecule: see text
Derivatized **6**	As for derivatized **5**	Reduction to ellagic acid (**5**) beforehand, see text

[a]for ^{31}P/^{1}H HMBC spectra, which confirm covalent derivatization, see Supplementary Material

[b]P resonances split due to homonuclear P–P coupling

usually so effective that no trace signals from solvent, water, NMMO, or amine degradation products of NMMO were observable in the spectra.

Gallic acid and its derivatives reacted neatly and quantitatively with the TMDP reagent to the corresponding phosphites, which gave clearly distinguishable product signals in all cases. The reaction conditions were based on procedures to derivatize (polymeric) lignins (Korntner et al. 2015a, b), which are usually sterically more demanding than the easily accessible low-molecular weight gallic acid derivatives. A threefold molar excess of TMDP reagent was used per hydroxy group to be derivatized, and a reaction time of 1 h at room temperature was used, which was in all cases sufficient to achieve complete conversion. Figure 2 displays the respective spectra and Table 1 gives the related ^{31}P NMR resonances of the derivatized compounds **1**–**5** (Zieher 2022). The ^{31}P NMR shifts were in the expected range of 130–150 ppm for derivatized phenolic OH groups. The successful derivatization was corroborated by ^{31}P/^{1}H HMBC spectra, which proved the long-range coupling between the P nucleus and the aromatic ring protons of the gallate moieties. The ^{31}P/^{1}H HMBC spectra of the phosphite derivatives, along with the complete resonance assignment in the ^{1}H and ^{13}C NMR domains, are given in the Supplementary Material. From the spectra, it was evident that the derivatization/^{31}P NMR approach, taken from the analysis of native and technical lignins, was well suited to detect and quantify the Lyocell stabilizers and their reaction products from Lyocell solutions.

Since the derivatized compounds contain more than one phosphite moiety, the ^{31}P resonances do not appear as singlets due to the long-range homonuclear P,P-coupling with a coupling constant of $^{5}J_{P,P}$ = 8 Hz (see Table 1). The P-atoms at former OH-3 and OH-5 in compounds **1**–**4** are magnetically equivalent (mirror symmetry) and thus give one resonance. The same applies to the P-atoms at the "opposite" hydroxy groups in the centrosymmetric ellagic acid (**5**). Under the derivatization conditions, in pyridine-d_5 as the solvent, the carboxy groups are not derivatized but form the corresponding pyridinium carboxylates. A minor resonance at 15–17 ppm is almost ubiquitous in the product spectra. It comes from a hydrolysis product of the derivatization agent, 4,4,5,5-tetramethyl-1,3,2λ^5-dioxaphospholan-2-one (Skarżyńska et al. 2011), see also Fig. 2. Spectroscopic data and the formation mechanism of the compound have been discussed in detail in a previous account (Zieher et al. 2023).

Conversion of the gallic acid derivatives to their phenolate salt forms, in an attempt to increase reactivity, is not only unnecessary but downright counterproductive: the phenolates become extremely sensitive to oxygen, which is reflected in dark discoloration of the solutions and the formation of undefined oligomerization products (note that pyrogallol, the decarboxylation product of gallic acid, is used in

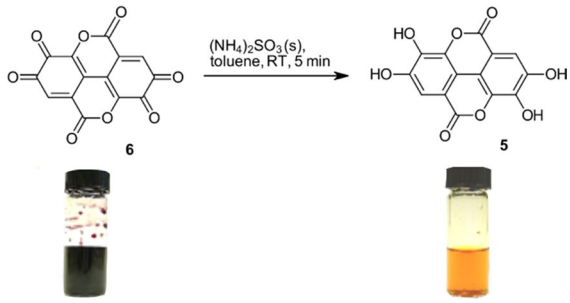


Fig. 3 Reduction of the dark-colored bis(*ortho*-quinone) **6** to yellowish ellagic acid (**5**) as a preliminary step to its indirect determination by the derivatization-^{31}P NMR approach

alkaline solution to free gases from oxygen traces). Moreover, the dry phenolates have a lower solubility in the NMR solvent than the free phenols. Finally, an alkaline medium to generate the phenolates also poses the risk of gallic acid esters being saponified and falsely detected as gallic acid.

In spinning dopes that have been subjected to prolonged aging or thermal stress, ellagic acid (**5**), the primary product of stabilization with gallic acid derivatives, is further oxidized to its bis(*ortho*-quinone) (**6**), a very strongly UV/VIS-absorbing compound of which a 10 µM aqueous ethanolic solution already appears black. The presence of **6** is often responsible for the dark discoloration of Lyocell spinning solutions. If the toluene extracts from these spinning dopes (see above) are dark colored, the presence of the bis(*ortho*-quinone) can be assumed—if, on the other hand, they are nearly colorless or yellow, its presence can be safely excluded. Compound **6**—which has no hydroxy groups—cannot be directly determined by the derivatization-^{31}P NMR method. To quantify its amount, the toluene extract is stirred with a small amount of solid ammonium sulfite (roughly 0.1 g/50 mL solution), which reduces the bis(*ortho*-quinone) into ellagic acid in less than a minute at RT (Fig. 3). This process can easily be tracked by the almost immediate brightening of the solution upon contact with the inorganic salt. The solids are filtered off and the derivatization is carried out as usual, indirectly detecting the bis-(*ortho*-quinone) as ellagic acid.

It is important to note that the derivatization agent must be applied in at least a threefold excess relative to the molar amount of hydroxy groups to

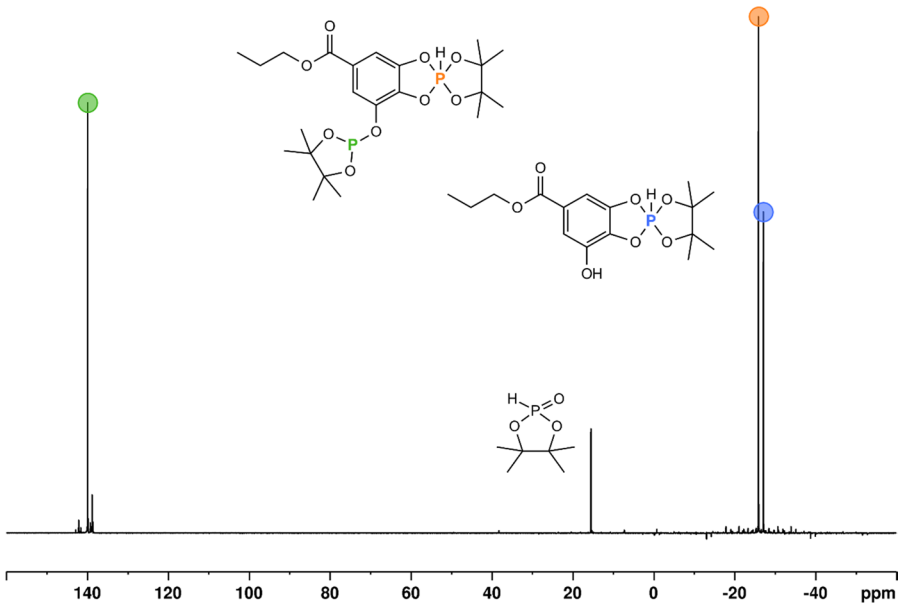


Fig. 4 Proton-decoupled ^{31}P NMR spectrum resulting from the phosphitylation of propyl gallate (**2**) with 2 molar eq. of TMDP (**7**) in deuterated pyridine and the correspondingly formed components. The phosphitylated OH group appears at + 139.89 ppm, the 1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nonane moieties from modified vicinal hydroxy groups at − 25.95 ppm (derivatized neighboring third OH group) and − 27.16 ppm (in case of a non-derivatized neighboring third OH group), and the hydrolysis product of **7** (Zieher et al. 2023) at + 15.48 ppm. NMR-solvent: C_5D_5N

be derivatized (estimated from the mass of extract), as otherwise, at a lower molar ratio, P-*spiro*-compounds, 1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nonane derivatives, are formed. Their formation mechanism starts with the derivatization of the most acidic OH group in the gallic acid derivatives, i.e., the OH in *para*-position to the carboxylic acid function, with TMDP. If the derivatization agent is not present in large excess, the nucleophilic attack of the gallate's neighboring hydroxy group at the P-atom in the already bound phospholane becomes competitive for the reaction with unreacted TMDP reagent, i.e., the intended intermolecular process is increasingly displaced by a parallel intramolecular process. Note that phosphorus, other than the elements in the second period of the periodic table of elements, is capable of valance shell extension. The result is the formation of a 1,4,6,9-tetraoxa-5λ^5-phosphaspiro[4.4]nonane derivative, or P-*spiro*-bis(phospholane), with the central phosphorus being in the P(III) oxidation state and carrying a directly bound H-atom, as seen by the heteronuclear $^1J_{P,H}$-coupling in the non-^{1}H-decoupled spectra as well as in the ^{1}H NMR spectra in form of a doublet-type signal (see Zieher et al. 2023). The remaining free hydroxy group at the gallate moiety can remain free or react with the derivatization reagent, if present, in the usual manner (Fig. 4).

Figure 4 shows the example spectrum of propyl gallate derivatized with insufficient excess of reagent. The formation of P-*spiro* compounds occurred similarly for all the other gallic acid derivatives if the excess of derivatization reagent was not high enough (see the Supplementary Material for the spectra of the P-*spiro* compounds and resonance assignments in the ^{31}P, ^{1}H, and ^{13}C domains). The ^{31}P NMR shift of the P-*spiro* compounds appeared in the shift range around −20 to −30 ppm and was thus very different from the "normally" derivatized phenolic OH groups (approx. + 140 ppm). Although the derivatization with less excess of reagent results in higher spectral complexity and does not yield a single product as the standard procedure does, it can be of analytical value. Because the chemical shifts of the regularly derivatized gallic acid derivatives fall within a fairly narrow range (+ 138 to 143 ppm), the occurrence of the P-*spiro* compounds (− 20 to − 30 ppm) provides additional opportunities to identify and quantify compounds or to verify the values obtained by the standard derivatization procedure.

Conclusions

The derivatization-^{31}P NMR method, known from hydroxy group quantification in lignin chemistry, was adapted to the analysis of gallic acid-derived stabilizers in Lyocell spinning dopes. These compounds are readily extractable and can be neatly derivatized with the phosphitylation reagent, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, **7**). At least a threefold molar excess of the reagent is required to hold the competitive formation of P-*spiro* compounds at bay. Derivatization is carried out in the NMR tube in perdeuterated pyridine, which serves multiple purposes as the NMR solvent, derivatization medium, catalyst, and HCl trap. Care needs to be taken to exclude water traces to avoid hydrolysis of the reagent and side reactions. The presented method offers an easy and fast approach for checking the stabilizer status in Lyocell dopes. It can help to correlate the concentration and type of gallate-derived byproducts with reaction conditions and process parameters. Therefore, we hope that the presented method will quickly become accepted as a new tool in Lyocell research and cellulosic fiber chemistry in general.

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Author contributions All authors contributed to the study's conception and design. Material preparation, data collection and analysis were performed by all authors. The first draft of the manuscript was written by TR. All authors commented on previous versions and read and approved the final manuscript.

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Availability of data and materials Data is available from the authors upon request.

Code availability Not applicable.

Declarations

Conflict of interest The authors declare no competing interests.

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication All authors agreed to the publication in the submitted form.

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