Key chromophores in celluloses

Zieher, Johanna; Bacher, Markus; Sulaeva, Irina; Sumerskii, Ivan; Hettegger, Hubert; Potthast, Antje; Rosenau, Thomas

Published in:
Cellulose

DOI:
10.1007/s10570-023-05184-x

Published: 01/06/2023

Document Version
Final published version

Document License
CC BY

Cellulose (2023) 30:5437–5445
https://doi.org/10.1007/s10570-023-05184-x

COMMUNICATION

Key chromophores in celluloses: analysis by ^{31}P NMR spectroscopy

Johanna Zieher · Markus Bacher · Irina Sulaeva · Ivan Sumerskii · Hubert Hettegger · Antje Potthast · Thomas Rosenau

Received: 3 February 2023 / Accepted: 3 April 2023 / Published online: 4 May 2023

Abstract The three cellulosic key chromophores, 2,5-dihydroxy-[1,4]-benzoquinone, 5,8-dihydroxy-[1,4]-naphthoquinone and 2,5-dihydroxy-acetophenone, are nearly ubiquitous in cellulosic materials because of their special structures and resonance stabilization with highly delocalized double bonds that renders them thermodynamically very stable and resistant towards bleaching. All of these compounds possess acidic hydroxyl groups. The current work explores the derivatization of these OH groups by a phosphitylation agent followed by ^{31}P NMR analysis, an approach that is very frequently used for quantitative OH group analysis and differentiation in lignins and lignin derivatives. The chemical shifts are reported and structural peculiarities of the chromophore derivatives are discussed. The ^{31}P NMR approach adds to the toolbox of methods applicable in cellulose chromophore analysis, bleaching and aging studies.

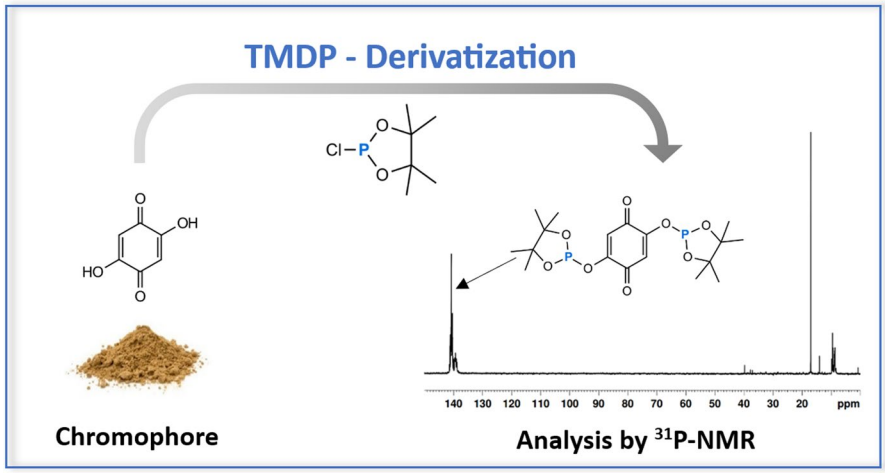
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10570-023-05184-x.

J. Zieher · M. Bacher · H. Hettegger · A. Potthast · T. Rosenau (✉)
Department of Chemistry, Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad-Lorenz-Straße 24, 3430 Tulln, Austria
e-mail: thomas.rosenau@boku.ac.at

I. Sulaeva · I. Sumerskii
Core Facility Analysis of Lignocellulosics (ALICE), University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad-Lorenz-Straße 24, 3430 Tulln, Austria

T. Rosenau
Faculty of Science and Engineering, Laboratory of Natural Materials Technology, Åbo Akademi University, Porthansgatan 3, 20500 Åbo/Turku, Finland

Graphical abstract

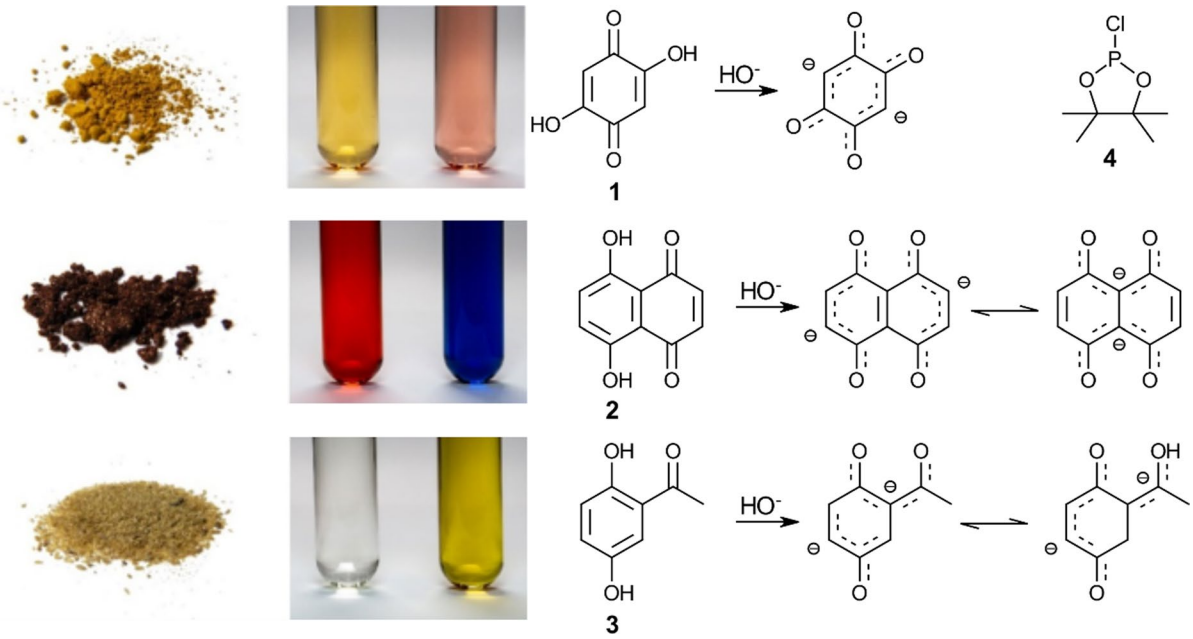


Keywords Aging · Bleaching · Brightness · Cellulose · Chromophore · Fibers · ^{31}P NMR spectroscopy · Paper · Yellowing

Introduction

The "chromophore release and identification" (CRI) methods provided access to trace chromophores in cellulosic materials which have been analyzed for different cellulose I and cellulose II substrates and cellulose derivatives (Rosenau et al. 2004). It provides isolated chromophoric compounds for detailed analytical characterization where spectroscopic methods only report likely structural motifs (Loureiro et al. 2010; Piantanida et al. 2005; Missori et al. 2019; Wójciak et al. 2014). In later work, it was established that some cellulosic chromophores are nearly ubiquitous because of their special stabilization by resonance. This causes strongly delocalized double bonds which leads to extremely low reactivity towards oxidative bleaching agents and high thermodynamic stability. This structural peculiarity renders these compounds prime survivors of standard bleaching sequences on the one hand, and the first chromophore candidates to reappear in yellowing/brightness reversion processes on the other hand (Korntner et al. 2015a; Ahn et al. 2019). The term "key chromophores" has thus been coined for these compounds, 2,5-dihydroxy-[1,4]-benzoquinone (DHBQ, **1**), 5,8-dihydroxy-[1,4]-naphthoquinone (DHNQ, **2**) and 2,5-dihydroxy-acetophenone (DHAP, **3**), and has become common terminology in the cellulose bleaching literature (Korntner et al. 2015a; Kumar et al. 2018; Hosoya et al. 2018). As the key chromophore structures, as a rule of thumb, make up between 50 and 75% of the overall isolable chromophores, there is a natural interest in methods to analyze and possibly quantify them in different cellulosic matrices. These analytical approaches are generally aggravated by the low concentration of the chromophores and often their presence in complex multi-component mixtures after CRI isolation.

The presence of relatively acidic hydroxyl groups is a common structural feature of the key chromophores. DHBQ with a pK_a of 2.71 (Hosoya et al. 2013), for instance, is significantly more acidic than acetic acid (pK_a 4.76). The proton release in these compounds is favored by the high stability (resonance) of the corresponding (di)anions (Scheme 1). The nature of the hydroxyl groups and the corresponding oxoanions resulting from deprotonation is hard to define formally. The resonance superposition of quinoid and aromatic canonic structures provides them with both quinoid and aromatic (phenolic) properties at the same time. Nevertheless, there is an obvious closeness to hydroxyl structures in lignins. In fact, DHBQ is a component in oxidized Kraft lignins (Musl et al. 2019). Apart from



Scheme 1 Cellulosic key chromophores DHBQ (**1**), DHNQ (**2**), and DHAP (**3**), their optical appearance as neat solids and in acidic (left) and alkaline (right) aqueous solution (approx. 1 mM), and chemical formula and structure of the resonance-stabilized dianions. Top right: structure of the derivatization agent 2-hydroxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (**4**) used for detection of acidic hydroxyl groups by ^{31}P NMR

aliphatic OH groups in the lignins´ side chains, there are various aromatic (phenolic) hydroxyl groups in the differently substituted aromatic systems (e.g., Balakshin and Capanema 2015; Balakshin et al. 2020). Quantitative analysis of these hydroxyl groups is commonly performed by ^{31}P NMR after derivatization with special phosphitylation reagents, according to an approach originally introduced by Argyropoulos (Argyropoulos et al. 1993; Argyropoulos 1994, 1995; Faix et al. 1994). Since then, the method has been very frequently used, comprehensively optimized and tested, and has become a standard technique for in-depth structural characterization of native and technical lignins with regard to their acidic hydroxyl groups, i.e., aliphatic and aromatic OH as well as carboxylic acid functionalities (Meng et al. 2019; Korntner et al. 2015b). For derivatization, typically the chlorophospholane reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, **4**) is used (Granata and Argyropoulos 1995), which neatly affords phosphites upon reaction with acidic hydroxyl groups. The procedure is particularly easy, mostly done in situ in the NMR tube, and the spectra can be well interpreted due to the high sensitivity of the ^{31}P isotope in NMR and the broad chemical shift range of this nucleus. While the main focus of the approach has always been on 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), it was later transferred also to the analysis of non-lignin substrates, such as polysaccharide derivatives, modified wood, or the elucidation of active agents in bleaching or glycosidation (Spyros et al. 1997; Fu et al. 2007; Argyropoulos et al. 2006; King et al. 2009, 2010; Hosoya et al. 2014; Sadeghifar et al. 2014). It was somehow obvious to test this derivatization also with the cellulosic key chromophores and to see whether the typical lignin ^{31}P NMR approach could become a useful tool also in the realm of cellulose analysis. For this, the respective ^{31}P NMR data of the standard key chromophore compounds—or, more correctly, their phosphite derivatives—were needed, which is the topic of the present communication.

Materials and methods

The used reagents and solvents were bought from commercial sources with a purity > 95% and, unless otherwise noted, used without further purification. NMR solvents were obtained from Sigma-Aldrich (Schnelldorf, Germany) or Eurisotop (Saint-Aubin, France). Glassware was dried in a vacuum oven. The derivatization agent TMDP was synthesized in-house.

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 probe head (Prodigy) with z-gradient at RT. Data processing was performed with the software Bruker Topspin 3.6.3. ^{1}H and ^{13}C 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. ^{31}P spectra were calibrated either externally on triphenylphosphine with δ (^{31}P) = − 20.1 ppm, or internally on residual TMDP reagent with δ (^{31}P) = − 175.3 ppm, respectively. For the ^{1}H,^{31}P-HMBC spectra a long-range coupling constant of ^{lr}J(P,H) = 5 Hz was used.

The derivatization method (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 (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, 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 into an NMR tube.

Results and discussion

Upon derivatization of the three key chromophores with the phospholane chloride, prominent and clearly distinguishable product peaks were obtained in all cases. It was obvious that all three chromophores reacted neatly with the reagent to give phosphite products with ^{31}P NMR resonances in the expected range, i.e., 130–150 ppm for derivatized phenolic OH groups. Interestingly, also the derivatized DHBQ appeared in this range although its hydroxyl groups are not phenolic but quinoid. ^{31}P,^{1}H-HMBC spectra proved the long-range coupling between the phosphorus and the methyl protons of the reagent as well as the ring protons of the chromophores, and thus the successful derivatization. These spectra, along with the ^{1}H and ^{13}C shift listings, are included in the Supplementary Information. Scheme 1 shows the structure

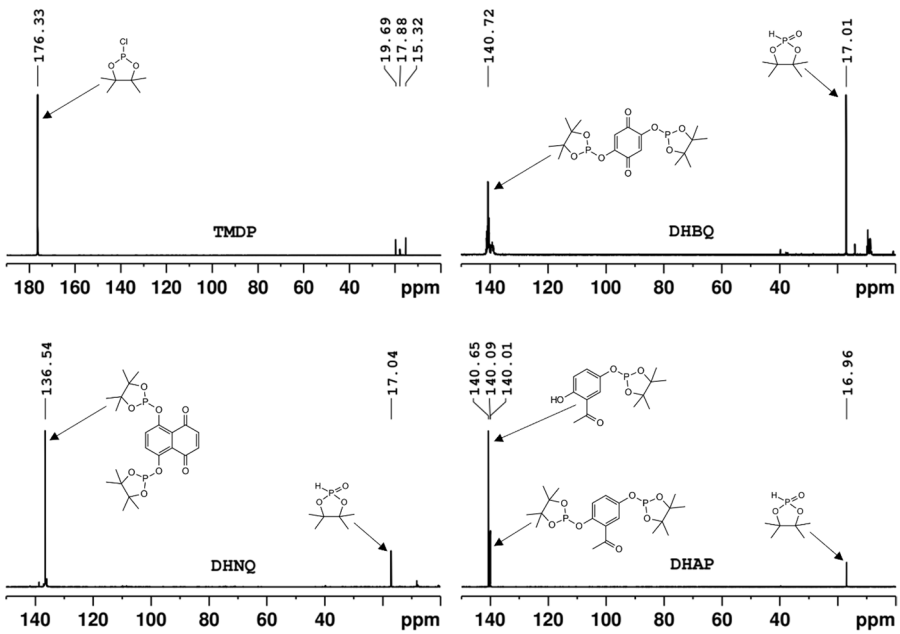


Fig. 1 Proton-decoupled ^{31}P NMR spectra of derivatization reagent (upper left) and the derivatized key chromophores DHBQ (**1**, upper right), DHNQ (**2**, lower left) and DHAP (**3**, lower right). For the hydrolysis product appearing at approx. 17 ppm, see below. Derivatization medium and NMR solvent: C_5D_5N (pyridine-d_5)

Table 1 ^{31}P NMR shifts (^{1}H-decoupled, in ppm) of derivatization reagent **4**, derivatized key chromophores **1–3** and byproduct **5**

Analyte	Chemical shift ^{31}P NMR (ppm)[a]	Remark
Reagent **4**	176.3	
Derivatized **1**	140.7	Minor byproducts around 138–139 ppm, see text
Derivatized **2**	136.5	
Derivatized **3**	140.6 (mono), 140.0/140.1 (bis)	For regioselectivity of the derivatization, see text
Byproduct **5**	around 17.0	For formation mechanism, see text

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

of the cellulosic key chromophores and the ^{31}P NMR derivatization agent, Fig. 1 displays the ^{31}P NMR spectra of the reagent and the three derivatized compounds, and Table 1 lists the corresponding ^{31}P NMR chemical shift values (Zieher 2022). It can thus be concluded that the derivatization/^{31}P NMR approach is generally well suited to detect the chromophores in compound mixtures of chromophores.

The derivatization conditions were based on procedures to derivatize natural and technical lignins which are sterically more hindered than the easily accessible, small chromophore molecules. A threefold to fivefold molar excess of the reagent relative to the sum of the hydroxy groups to be derivatized was used. Perdeuterated pyridine was the solvent of choice because of the good solubility of the compounds and also for trapping of the HCl generated in the derivatization reaction yielding pyridinium hydrochloride as soluble byproduct. Evidently, protic solvents cannot be used as they would react with the derivatization agent. In addition, DHBQ's 3-H and 6-H would undergo H–D exchange so that the corresponding cross-peaks in correlated spectra would "disappear" (Hosoya et al. 2013).

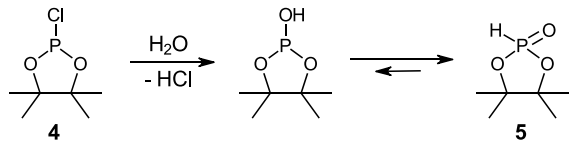
Regarding the application of the analytical method in practice, two notes are warranted here. First, this analytical approach targets chromophore mixtures obtained according to the CRI chromophore isolation method or alternative extraction procedures developed for cellulosic materials containing no or very little lignin, such as highly bleached pulps, bacterial cellulose or cotton (Rosenau et al. 2007, 2011, 2014). Chromophore mixtures from lignin-rich matrices can evidently not be analyzed with regard to the presence of individual components, because the chromophore resonances would be overrun from the predominant signals from the (residual) lignin: the ^{31}P NMR shift range around 140 ppm is typical of derivatized phenolic compounds. Instead, sum parameters for the different types of hydroxyl groups would be obtained, similar to the application of the ^{31}P NMR method in lignin chemistry. Second, the resonances of derivatized DHBQ and DHAP are too close to allow discrimination (Table 1). However, the shift of derivatized DHNQ, which differs significantly from those of the former (ca. 4 ppm), offers an interesting way to distinguish this chromophore in mixtures: hemicellulose precursors generate all three chromophores upon aging whereas cellulose forms only DHBQ and DHAP, but no DHNQ (Zwirchmayr et al. 2017). ^{31}P NMR could help to better define the "provenance" and "history" of chromophores in cellulosic matrices which has remained an unsolved problem.

The main peak from the derivatized DHBQ was accompanied by minor resonances. These come from rearrangement and polymerization side products in small amounts (< 5%) which are almost ubiquitous companions of DHBQ unless it is strictly kept under an inert atmosphere. DHAP gave always rise to two signals, one from the mono-derivatized and one from the bis-derivatized product. Even at high excess of the derivatization reagent, the mono-substituted product was still present. Mono-derivatization occurred regioselectively at OH-5 because OH-2 is engaged in a very stable hydrogen bond to the carbonyl oxygen of the adjacent acetyl group and consequently showed rather a low acidity and reactivity in the derivatization. This behavior is well known from polyphenols with *ortho*-acyl substituents, e.g., flavonoids or vitamin E derivatives (Rosenau et al. 2005), and can—by using low temperatures and suitable solvents—even be exploited in chemical synthesis for a highly selective distinction of the hydroxyl functions.

The key chromophores should not be converted into their anions (salts) in an attempt to increase the rate of the derivatization, for three reasons. First, the

derivatization process is quite fast anyway and reliably completed after 30 min. The used reaction time of 1 h adds additional time for complete derivatization. Second, the corresponding salts would be difficult to dry and much harder to dissolve in the NMR solvent. Third, derivatization of the anions causes byproduct formation, in particular reactions under C-P coupling, which becomes understandable from the resonance structures with their increased C-nucleophilicity (see Scheme 1).

One by-product with a resonance at about 17 ppm (Table 1) deserves some attention since it was found in all spectra of the derivatized compounds without exception. The compound, 4,4,5,5-tetramethyl-1,3,2λ^5-dioxaphospholan-2-one, possesses the five-membered 1,3,2-dioxaphospholane ring of the derivatization reagent, but—in addition—a double-bonded oxygen and a hydrogen bound to the phosphorus atom (Skarżyńska et al. 2011). The ^{1}H/^{31}P-HMBC spectrum in Fig. 2 illustrates the coupling between the H atom (orange) and the P-atom (blue) of the compound, with a characteristic coupling constant of $^{1}J = 704$ Hz. This ^{31}P doublet appears also in the non-^{1}H-decoupled ^{31}P spectra with the same coupling constant.



Scheme 2 Formation of the hydrolysis product 4,4,5,5-tetramethyl-1,3,2λ^5-dioxaphospholan-2-one (**5**) from derivatization reagent **4**

It should be noted that this compound is not a true oxidation product of the reagent, formed by the unavoidable contact with atmospheric oxygen, as it might appear at first glance from the P=O motif. Instead, it is simply the hydrolysis product: contact of the reagent with trace amounts of water results in the formation of 2-hydroxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, which immediately forms 4,4,5,5-tetramethyl-1,3,2λ^5-dioxaphospholan-2-one (**5**) by a [1,2]-sigmatropic proton shift (Scheme 2). Formally, both compounds can be considered as

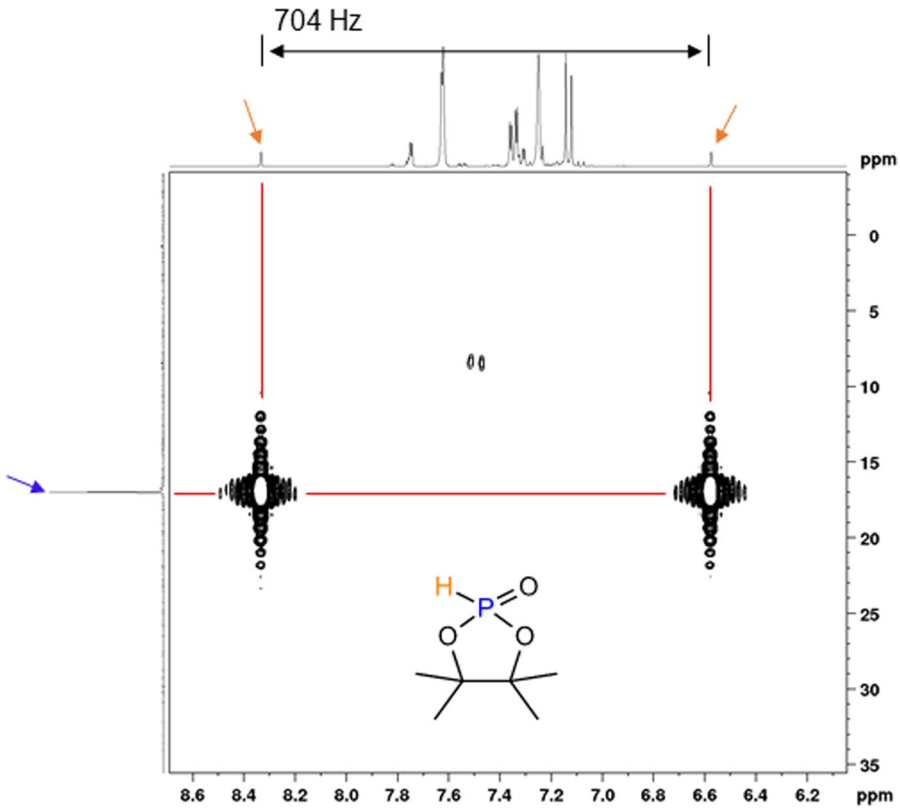


Fig. 2 Hydrolysis product **5** and its ^{1}H (x-axis)/^{31}P (y-axis) HMBC-spectrum, showing the ^{1}J coupling of 704 Hz between the H atom (orange) and the P atom (blue). This spectrum originates from the phosphitylation of DHAP (**3**), but **5** was also found in all other reaction mixtures

tautomers (Janesko et al. 2015), with the equilibrium between the two compounds far on the side of the pentavalent phosphorus ($K = 2 \times 10^{10}$, Guthrie 1979). However, the O,P-sigmatropic H-shift also implies an intramolecular redox process in which phosphorus is oxidized from + III to + V, while H is being reduced from + 1 to − 1. The compound is an organic diester of phosphorous acid, which is a diprotic acid (H_3PO_3, with one H being bound directly to P as $O=PH(OH)_2$). This is different from its P(V) counterpart, the triprotic phosphoric acid (H_3PO_4, corresponding to $O=P(OH)_3$).

Conclusions

The three cellulosic key chromophores can be neatly derivatized using the phosphitylation reagent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (**4**), which is very well-known from lignin analysis. The reaction is carried out in the NMR tube in perdeuterated pyridine, which serves simultaneously as the derivatization medium, catalyst, HCl trap and NMR solvent. The presence of water or other protic solvents would interfere with the derivatization. We hope that this easy derivatization in combination with ^{31}P NMR will be well accepted as a useful tool in chromophore research and become as widely used as in lignin analysis.

Acknowledgments We would like to thank the University of Natural Resources and Life Sciences, Vienna (BOKU) and the County of Lower Austria for their financial support through the framework of the Austrian Biorefinery Center Tulln (ABCT).

Author contributions All authors contributed to the study 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.

Funding Open access funding provided by University of Natural Resources and Life Sciences Vienna (BOKU). The financial support by the Austrian Biorefinery Center Tulln (ABCT) is gratefully acknowledged.

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

Code availability Not applicable.

Declarations

Conflict of interest The authors have not disclosed any conflict of interest.

Consent to participate Not applicable.

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

Ethics approval Not applicable.

References

Ahn K, Zaccaron S, Zwirchmayr NS, Hettegger H, Hofinger H, Bacher M, Henniges U, Hosoya T, Potthast A, Rosenau T (2019) Yellowing and brightness reversion of celluloses: CO or COOH, who is the culprit? Cellulose 26:429–444

Akim LG, Argyropoulos DS, Jouanin L, Leplé JC, Pilate G, Pollet B, Lapierre C (2001) Quantitative ^{31}P NMR spectroscopy of lignins from transgenic poplars. Holzforschung 55(4):386–390

Argyropoulos DS (1994) Quantitative phosphorus-31 nmr analysis of lignins, a new tool for the lignin chemist. J Wood Chem Technol 14(1):45–63

Argyropoulos DS (1995) ^{31}P NMR in wood chemistry: a review of recent progress. Res Chem Intermed 21(3–5):373–395

Argyropoulos DS, Zhang L (1998) Semiquantitative determination of quinonoid structures in isolated lignins by ^{31}P nuclear magnetic resonance. J Agric Food Chem 46(11):4628–4634

Argyropoulos DS, Bolker HI, Heitner C, Archipov Y (1993) ^{31}P NMR spectroscopy in wood chemistry. Part V. Qualitative analysis of lignin functional groups. J Wood Chem Technol 13(2):187–212

Argyropoulos DS, Li H, Gaspar AR, Smith K, Lucia LA, Rojas OJ (2006) Quantitative ^{31}P NMR detection of oxygen-centered and carbon-centered radical species. Bioorg Med Chem 14(12):4017–4028

Balakshin MY, Capanema EA (2015) Comprehensive structural analysis of biorefinery lignins with a quantitative ^{13}C NMR approach. RSC Adv 5:87187–87199

Balakshin M, Capanema EA, Zhu X, Sulaeva I, Potthast A, Rosenau T, Rojas OJ (2020) Spruce milled wood lignin: Linear, branched or cross-linked? Green Chem 22(13):4985–4001

Crestini C, Argyropoulos DS (1997) Structural analysis of wheat straw lignin by quantitative ^{31}P and 2D NMR spectroscopy. The occurrence of ester bonds and α-*O*-4 substructures. J Agric Food Chem 45(4):1212–1219

Faix O, Argyropoulos DS, Robert D, Neirinck V (1994) Determination of hydroxyl groups in lignins evaluation of 1H–13C-, 31P-NMR, FTIR and wet chemical methods. Holzforschung 48(5):387–394

Fu Q, Argyropoulos DS, Tilotta DC, Lucia LA (2007) Products and functional group distributions in pyrolysis oil of chromated copper arsenate (CCA)-treated wood, as elucidated by gas chromatography and a novel ^{31}P NMR-based methods. Ind Engin Chem Res 46(16):5258–5264

Granata A, Argyropoulos DS (1995) 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins. J Agric Food Chem 43(6):1538–1544

Guerra A, Norambuena M, Freer J, Argyropoulos DS (2008) Determination of arylglycerol-β-aryl ether linkages in enzymatic mild acidolysis lignins (EMAL): comparison of DFRC/^{31}P NMR with thioacidolysis. J Nat Prod 71(5):836–841

Guthrie JP (1979) Tautomerization equilibria for phosphorous acid and its ethyl esters, free energies of formation of phosphorous and phosphonic acids and their ethyl esters, and p Ka values for ionization of the P–H bond in phosphonic acid and phosphonic esters. Can J Chem 57(2):236–239

Hosoya T, French AD, Rosenau T (2013) Chemistry of 2,5-dihydroxy-[1,4]-benzo-quinone, a key chromophore in aged cellulosics. Mini-Rev Org Chem 10(3):309–315

Hosoya T, Takano T, Kosma P, Rosenau T (2014) Theoretical foundation for the presence of oxacarbenium ions in chemical glycoside synthesis. J Org Chem 79(17):7889–7894

Hosoya T, Bacher M, Potthast A, Elder T, Rosenau T (2018) Insights into degradation pathways of oxidized anhydroglucose units in cellulose by β-alkoxy-elimination—a combined theoretical and experimental approach. Cellulose 25(7):3797–3814

Janesko BG, Fisher HC, Bridle MJ, Montchamp JL (2015) P(=O)H to P-OH tautomerism: a theoretical and experimental study. J Org Chem 80(20):10025–10032

Jiang ZH, Argyropoulos DS (1998) Coupling P-31 NMR with the Mannish reaction for the quantitative analysis of lignin. Can J Chem 76(5):612–622

King AWT, Zoia L, Filpponen I, Olszewska A, Haibo XIE, Kilpeläinen I, Argyropoulos DS (2009) In situ determination of lignin phenolics and wood solubility in imidazolium chlorides using ^{31}P NMR. J Agric Food Chem 57(18):8236–8243

King AWT, Jalomäki J, Granström M, Argyropoulos DS, Heikkinen S, Kilpeläinen I (2010) A new method for rapid degree of substitution and purity determination of chloroform-soluble cellulose esters, using ^{31}P NMR. Anal Meth 2(10):1499–1505

Korntner P, Hosoya T, Dietz T, Eibinger K, Reiter H, Spitzbart M, Röder T, Borgards A, Kreiner W, Mahler AK, Winter H, French AD, Henniges U, Potthast A, Rosenau T (2015a) Chromophores in lignin-free cellulosic materials belong to three compound classes. Cellulose 22(2):1053–1062

Korntner P, Sumerskii I, Bacher M, Rosenau T, Potthast A (2015b) Characterization of technical lignins by NMR spectroscopy: optimization of functional group analysis by ^{31}P NMR spectroscopy. Holzforschung 69(6):807–814

Kumar A, Cardia R, Cappellini G (2018) Electronic and optical properties of chromophores from bacterial cellulose. Cellulose 25(4):2191–2203

Loureiro PEG, Fernandes AJS, Carvalho MGVS, Evtuguin DV (2010) The assessment of chromophores in bleached cellulosic pulps employing UV-Raman spectroscopy. Carbohydr Res 345(10):1442–1451

Meng X, Crestini C, Ben H, Hao N, Pu Y, Ragauskas AJ, Argyropoulos DS (2019) Determination of hydroxyl groups in biorefinery resources via quantitative ^{31}P NMR spectroscopy. Nat Protocols 14(9):2627–2647

Missori M, Mosca Conte A, Pulci O, Teodonio L, Dominijanni S, Puteo S, Iannuccelli S, Sotgiu S, Sebastiani ML (2019) Non-destructive monitoring of molecular modifications in the restoration of works of art on paper: application of theoretical and experimental optical spectroscopy. Eur Phys J plus 134(3):99

Musl O, Holzlechner M, Winklehner S, Guebitz G, Potthast A, Rosenau T, Böhmdorfer S (2019) Changing the molecular structure of kraft lignins—ozone treatment at alkaline conditions. ACS Sust Chem Engin 7(18):15163–15172

Piantanida G, Bicchieri M, Coluzza C (2005) Atomic force microscopy characterization of the ageing of pure cellulose paper. Polymer 46(26):12313–12321

Rosenau T, Potthast A, Milacher W, Hofinger A, Kosma P (2004) Isolation and identification of residual chromophores in cellulosic materials. Polymer 45(19):6437–6443

Rosenau T, Ebner G, Stanger A, Perl S, Nuri L (2005) From a theoretical concept to biochemical reactions: strain induced bond localization (SIBL) in oxidation of vitamin E. Chem Eur J 11(1):280–287

Rosenau T, Potthast A, Kosma P, Suess HU, Nimmerfroh N (2007) First isolation and identification of residual chromophores from aged bleached pulp samples. Holzforschung 61(6):656–661

Rosenau T, Potthast A, Krainz K, Yoneda Y, Dietz T, Shields ZPI, French AD (2011) Chromophores in cellulosics, VI. First isolation and identification of residual chromophores from cotton linters. Cellulose 18(6):1623–1633

Rosenau T, Potthast A, Krainz K, Hettegger H, Henniges U, Yoneda Y, Rohrer C, French AD (2014) Chromophores in cellulosics, XI. Isolation and identification of residual chromophores from bacterial cellulose. Cellulose 21(4):2271–2283

Saake B, Argyropoulos DS, Beinhoff O, Faix O (1996) A comparison of lignin polymer models (DHPs) and lignins by ^{31}P NMR spectroscopy. Phytochem 43(2):499–507

Sadeghifar H, Dickerson JP, Argyropoulos DS (2014) Quantitative ^{31}P NMR analysis of solid wood offers an insight into the acetylation of its components. Carbohydr Polym 113:552–560

Skarżyńska A, Trzeciak AM, Gniewek A (2011) 4,4,5,5-Tetramethyl-1,3,2λ-dioxa-phospho-lan-2-one. Acta Crystallogr Sect E Struct Rep Online 67(8):o2159

Spyros A, Argyropoulos DS, Marchessault RH (1997) Study of poly(hydroxyalkanoate)s by quantitative ^{31}P NMR spectroscopy: molecular weight and chain cleavage. Macromol 30(2):327–329

Tohmura SI, Argyropoulos DS (2001) Determination of arylglycerol-β-aryl ethers and other linkages in lignins using DFRC/31P NMR. J Agric Food Chem 49(2):536–542

Wójciak A, Kasprzyk H, Sikorska E, Krawczyk A, Sikorski M, Wesełucha-Birczyńska A (2014) FT-Raman, FT-infrared and NIR spectroscopic characterization of oxygen-delignified kraft pulp treated with hydrogen peroxide under acidic and alkaline conditions. Vib Spectr 71:62–69

Zieher J (2022) Derivatization-NMR techniques in the analysis of lignocellulosics. Master thesis. University of Natural Resources and Life Sciences, Vienna (BOKU), Austria

Zinovyev G, Sulaeva I, Podzimek S, Rössner D, Kilpeläinen I, Sumerskii I, Rosenau T, Potthast A (2018) Getting closer to absolute molar masses of technical lignins. Chem Sus Chem 11(18):3259–3268

Zwirchmayr NS, Hosoya T, Hettegger H, Bacher M, Krainz K, Yoneda Y, Dietz T, Henniges U, Potthast A, Rosenau T (2017) Chromophores from hexeneuronic acids—chemical behavior under peroxide bleaching conditions. Cellulose 24(9):3689–3702