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Polymer 45 (2004) 6437–6443
polymer
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Isolation and identification of residual chromophores in cellulosic materials

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Received 10 March 2004; received in revised form 12 July 2004; accepted 15 July 2004

Abstract

A general procedure was developed for the isolation of residual chromophores in or on cellulosic material, which were hitherto inaccessible to structure elucidation due to their extremely low content in the ppb concentration scale. It is applicable to cellulosic pulp, cellulosic fibers (viscose, Lyocell) and cellulose derivatives (acetate, carbonyl-labeled cellulose) as well. The chromophore identification comprises treatment of the cellulosic material with boron trifluoride–acetic acid complex ($BF_3 \cdot 2HOAc$) containing sulfite, chromatographic separation of the resulting chromophore-containing mixture, and structure determination of the main constituents by NMR/MS and comparison to authentic samples. Both adsorbed and covalently bound aromatic and quinoid compounds are selectively released by the treatment. Covalent ester, ether and secondary alkyl links between chromophore and cellulose are broken.

Four cellulosic example substrates have been analyzed for their chromophore content: Lyocell fibers, cellulose triacetate, pulp after thermal treatment in *N*,*N*-dimethylacetamide, and pulp containing carbonyl-selective labels, and up to 11 chromophores per sample have been identified.

Keywords: Cellulose; Chromophores; Fibers

1. Introduction

The cellulose material in cellulosic fibers (viscose, Modal, Lyocell) or cellulose derivatives (esters, ethers, nitrates) has undergone a large number of process steps. The general process stages of pulping and bleaching, which are required to provide the starting cellulose free from non-cellulosic wood components, are followed by the process-specific manufacturing steps. Apart from chemically pure cellulose, as for instance present in bacterial cellulose, cellulosic pulps, fibers and derivatives contain minute amounts of chromophoric compounds. These chromophores either originate from the starting pulp, or they are newly formed during the subsequent processing stages of fiber formation or derivatization. The concentration of these chromophores is generally extremely low, mostly in the ppb range. However, due to their high extinction coefficient, the chromophores are nevertheless easily noticed as an off-white discoloration or yellowing effect, especially as the human eye is very sensitive in the yellow spectral range. The chromophore content was so far quantified as brightness, which—as a parameter inversely related to yellowing—was measured as UV absorbance at 457 nm [1].

So far, the chemical nature of the chromophores in cellulosic fibers and derivatives was largely unclear. The chemical identification of the trace compounds is rendered difficult by their low concentrations and by the large number of different compounds contributing to the overall discoloration effect. In addition, the chromophores might be bound to the cellulose matrix in different ways, either covalently or just simply by adsorption, and they might be present in different locations, either on the surface or in the interior. Isolation and chemical identification of individual chromophores in cellulosic materials has not been described so far.

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0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.07.031

In this study, we wish to communicate a novel chemo-analytical approach, by which it now became possible to selectively release aromatic and quinoid chromophores from cellulosic materials, which were subsequently separated and analyzed.

Considering the consumer notion—especially in body textiles, non-wovens and the medicare products—that only 'really white' materials are clean, the economic relevance of the chromophore issue for the pulp, paper and textile industries becomes obvious. A thorough knowledge of the chemical structure of these sub-ppm impurities in cellulosic fibers and products will allow devising better approaches to effective and smooth chromophore removal or destruction. Similarly, it will help to develop strategies to reduce chromophore formation in the different processes from the beginning, and thus to save bleaching costs.

2. Experimental

2.1. General

All chemicals were available from commercial suppliers and of the highest purity available. Sodium sulfite was finely powdered shortly before use.

A bleached beech sulfite pulp (kappa number 0.36, ISO brightness 87.8, carbonyl content 23.8 μmol g^{-1}, cuen viscosity 565, M_n 41.27, M_w 289.8) [2] was used for thermal treatment in DMAc and for CCOA labeling, and was also the starting material for the production of Lyocell fibers. Carbonyl-selective labeling of the pulp with CCOA was performed as described previously [3]. A cotton linters sample was used for the thermal treatment experiments in DMAc. Cellulose triacetate was available from Sigma-Aldrich chemical company.

2.2. Chromophore extraction with $BF_3 \cdot 2HOAc$

In a round-bottom flask, the cellulosic material (50–100 g) and sodium sulfite (0.50 g) were suspended in BF_3–acetic acid complex (150 ml) and methylene chloride (350 ml). The vessel was closed and shaken at room temperature for 48 h. The solids were separated on a filter, pressed out and washed with small amounts of glacial acetic acid. The organic phases were combined, and the pressing–washing cycles were repeated until the solids appeared bright white. After addition of methylene chloride (100 ml) containing α-tocopherol (vitamin E, 1.00 g), water (1.00 l) was added, and the mixture was vigorously shaken. After phase separation, the extraction of the aqueous phase by CH_2Cl_2 (100 ml) was repeated four times. The combined organic extracts were washed carefully with water and dilute aqueous $NaHCO_3$ solution until acid-free, and were dried over Na_2SO_4. The organic phase was evaporated in vacuo at r.t. to a volume of about 5 ml. Higher temperatures must be avoided as they promote condensation reactions. MeOH (50 ml) and 2 ml of 2 M ethereal HCl were added. The mixture was refluxed for 5 min, cooled to r.t., and evaporated. The dark oily residue was chromatographed on basic aluminum oxide (Brockmann grade I). Elution was performed with *n*-hexane to remove the stabilizer and polymeric, highly condensed chromophores, followed by ethyl acetate/toluene (v/v = 1:9), ethyl acetate and ethyl acetate/methanol (v/v = 1:1). The fractions were analyzed by MS and NMR, the latter only in the case of sufficient material available. Unambiguous identification of the compounds was accomplished by comparison with authentic compound samples, which were either commercially available, or synthesized according to standard techniques.

In the case of materials soluble or swelling in the extraction medium the following procedure was used: In a round-bottom flask, the cellulosic material (50–100 g) and sodium sulfite (0.50 g) were suspended in BF_3–acetic acid complex (150 ml) and glacial acetic acid (50 ml). The vessel was closed and shaken at room temperature for 48 h. *n*-Hexane (300 ml) was added to the heterogeneous mixture, and the mixture was vigorously shaken for 10 min. The *n*-hexane phase was removed, and the heterogeneous acetate phase was extracted twice with *n*-hexane (100 ml). After addition of methylene chloride (100 ml) containing α-tocopherol (vitamin E, 1.00 g), the combined *n*-hexane phases were carefully washed with water and diluted aqueous $NaHCO_3$ solution until acid-free, and dried over Na_2SO_4. The further work-up and chromophore isolation followed the above procedure.

3. Results and discussion

3.1. Chromophore isolation by $BF_3 \cdot 2HOAc$—general aspects

Chromophores in/on cellulosic materials generally proved to be completely resistant towards extraction with various organic solvents, regardless of being polar, non-polar, protic or non-protic. This indicated either a covalent link of the chromophores to the fibers, or at least strong adsorptive binding. In preliminary experiments, we used methanol containing gaseous HCl for chromophore release, which provided a mixture of compounds in the ppb concentration range. However, this extraction procedure was unable to completely release chromophoric substances from the fibers, as easily seen by visual inspection. The UV spectrum of the extract reversibly changed upon reduction and exposure to air, accompanied also by a clearly visible color change between brown and faint yellow. This was indicative of the presence of phenolic compounds, which underwent phenol-to-quinone conversions and oxidative coupling reactions. We therefore searched for a method that was able to specifically release aromatics from complex matrices, largely independent of how the aromatic was attached.

For that purpose, the cellulosic material was treated with boron trifluoride–acetic acid complex, $BF_3 \cdot 2HOAc$, containing small amounts of sodium sulfite. This reagent cleaves ester and ether and carbon–carbon bonds extending from aromatic systems, due to its high complexation tendency with the electron-rich aromatic systems. Quinoid systems are reductively converted into the corresponding aromatics [4], and then similarly released. The sulfite present generates a reducing medium both in the extract and in the contacting gaseous phase due to the slow release of SO_2. Thus, oxygen is barred from entering the extraction solvent and phenol oxidation or coupling is prevented so that the nature of the released chromophores is preserved and a nearly colorless extract resulted. An additional benefit with regard to oxidative stability during extraction is the fact that phenolic and aliphatic hydroxyls are acetylated, giving acetates. The reactions brought about by $BF_3 \cdot 2HOAc$ treatment are schematically summarized in Fig. 1. After separation of the released chromophores from the extraction mixture, a hydrolytic step can be used to improve further chromatographic separation: treatment with gaseous HCl in MeOH regenerated the free hydroxyls by cleaving the acetates.

To demonstrate that the chromophores are not artifacts produced during the release/extraction procedure by the action of the Lewis-acidic reagent, a cotton linters sample was used as a blank: no chromophores were isolated in this case. In addition, also the extract from a second, prolonged $BF_3 \cdot 2HOAc$-treatment of cellulosic materials [5] provided no chromophores in isolable amounts. This confirmed on one hand that no 'new' chromophores were generated during this subsequent treatment, and demonstrated on the other hand that the release after the first treatment was quite complete. For Lyocell fibers, it was shown that the chromophoric compounds isolated were independent of the pulp source. Lyocell materials from either a bleached beech sulfite pulp (Section 2) or a bleached Eucalyptus prehydrolysis kraft pulp afforded the same chromophores, confirming that the chromophores isolated were formed in later processing stages, but were not contained in the pulps from the beginning. This result cannot be generalized, since especially for pulps containing residual lignins or large amount of hemicelluloses the structure and number of chromophores generated could well be different.

3.2. Chromophore isolation from different cellulosic materials

3.2.1. Lyocell fibers

Lyocell fibers are the product of the modern, environmentally benign Lyocell technology, according to which cellulose is directly dissolved in a melt of *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) at about 100 °C, giving a tractable spinning dope that is spun into air and water. The amine *N*-oxide is able to dissolve cellulose without the need of any chemical derivatization, and acts thus as a physical, recyclable and environmentally fully compatible cellulose solvent. Due to side reactions in the spinning dope between the strongly oxidizing solvent NMMO and the solute cellulose [6], Lyocell material contains trace amounts of chromophores, which might impair the brightness properties of the resulting fibers.

Using the above chromophore isolation procedure, six compounds as shown in Fig. 2 were determined in the extract from standard Lyocell fibers. Lyocell material which had suffered prolonged NMMO treatment (2 h in NMMO at 130 °C or 24 h in NMMO at 100 °C)—and thus exhibited an increased chromophore content—contained additional chromophores (Fig. 2). For the eleven compounds in Fig. 2 and for all those reported in the following, identification was based on the NMR (^1H and ^{13}C) and MS spectra, and on comparison with authentic samples.

Compounds **1–5** are typical condensation products obtained from carbohydrates upon either thermal, acidic or basic treatment [7]. They have been formed by cellulose degradation during the thermal conditions of Lyocell processing [8], and can be considered as primary chromophores. In the material having undergone prolonged thermal treatment in NMMO, these chromophores formed more highly condensed chromophoric structures **7–11** (secondary chromophores) under the prevailing more drastic and oxidative conditions. The compounds **6–8** and **11** proved

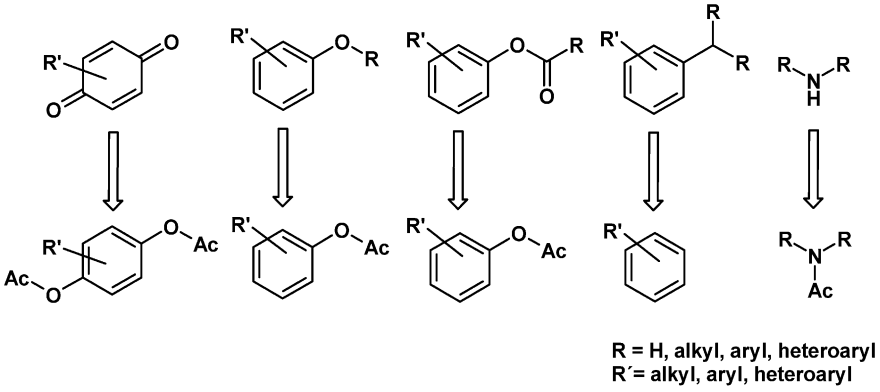

Fig. 1. Reactions proceeding upon chromophore release.

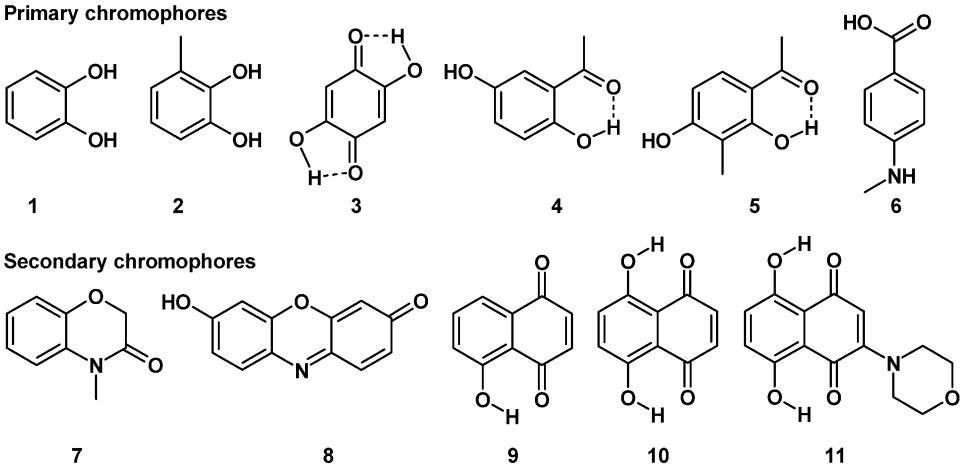

Fig. 2. Chromophores isolated from Lyocell fibers.

the participation of NMMO or NMMO degradation products, respectively, in chromophore generation. These compounds contained nitrogen, of which NMMO was the only possible source.

It should be mentioned that 2,5-dihydroxybenzoquinone (**3**) is rather stable, so that its reduction to 1,2,4,5-tetrahydroxybenzene requires conditions more drastic than the mildly reductive medium during chromophore isolation. This stability is due to two strong hydrogen bridges in acidic and neutral media, and due to pronounced resonance stabilization in alkaline media: the four oxygen atoms of the dianion become equivalent. It has long been known that alkaline, acidic, or thermal treatment of monosaccharides and also of cellulose in the presence of oxygen or other oxidants gives rise to EPR-active species after only a few minutes reaction time. The most prominent of the radicals produced is 2,5-dihydroxysemiquinone [9], which upon further oxidation readily affords **3**. This compound, which was found in all cellulosic materials investigated so far, can be seen as a basic 'chromophore precursor structure', which can on the one hand readily be degraded to smaller, reactive fragments, but on the other hand can also easily condense to larger structures, so that in any case other chromophores and highly condensed structures are formed from **3** by a complex interplay of fragmentation/condensation sequences.

3.2.2. Cellulose thermally 'activated' in N,N-dimethylacetamide

Cellulose samples of higher molecular weight are mostly insoluble in *N*,*N*-dimethylacetamide (DMAc)/lithium chloride, which is a very common solvent system widely used in gel chromatographic analysis of cellulosics. According to a common protocol, a so-called 'activation' by heating or refluxing these samples in DMAc is supposed to facilitate subsequent dissolution. In previous work, we have shown that such a treatment will cause degradation of the cellulosic material (which eventually causes the dissolution effect), and have been able to address the degradation mechanism and the nature of the chromophores in the DMAc solution [10]. However, the analysis of chromophores remaining bound to the pulp was beyond the capabilities at that time. Also light- and heat-induced yellowing of pulp (in the absence of DMAc) was attributed to the formation of furanoid structures, but also without isolation of defined compounds [11].

According to the novel chromophore isolation method, the chromophores **1**, **3**, **4**, **9**, and **12**–**17** were isolated from pulp, which had been heated in DMAc under reflux for 5 h, and then thoroughly washed. As shown in Fig. 3, the chromophores—except **14** and **15**—isolated are structurally very similar to the chromophores found in Lyocell fibers, or even identical. This is an additional indication of the fact that those chromophores are formed from cellulose by thermal stress, largely independent of the reaction medium. Besides these solely carbohydrate-based chromophores, also compounds generated in condensation reactions of DMAc without participation of cellulose were found, such as dehydroacetic acid (**14**) and isodehydroacetic acid *N*,*N*-dimethylamide (**15**). These two compounds were likely to be bound as ethers to cellulose, before being released by the BF_3 treatment. Chromophores **16** and **17** are formed by thermally induced condensation reactions between cellulose and solvent or, more specifically, by reaction of cellulose-derived primary chromophores **4** and **13** with the solvent. Interestingly, furan **18**, which was found as the major dissolved degradation product of cellulose in heated DMAc, was not detected as bound to the cellulose material. This confirmed the previously established thermal endwise-peeling mechanism during thermal treatment of cellulosic pulp in DMAc [10]: the furan does not remain bound to the cellulose matrix, but is immediately released into the solvent upon its formation.

3.2.3. Cellulose triacetate

A modified variant of the extraction procedure (Section 2) was used to identify residual chromophores in cellulose triacetate, as the material was semisoluble in the extraction

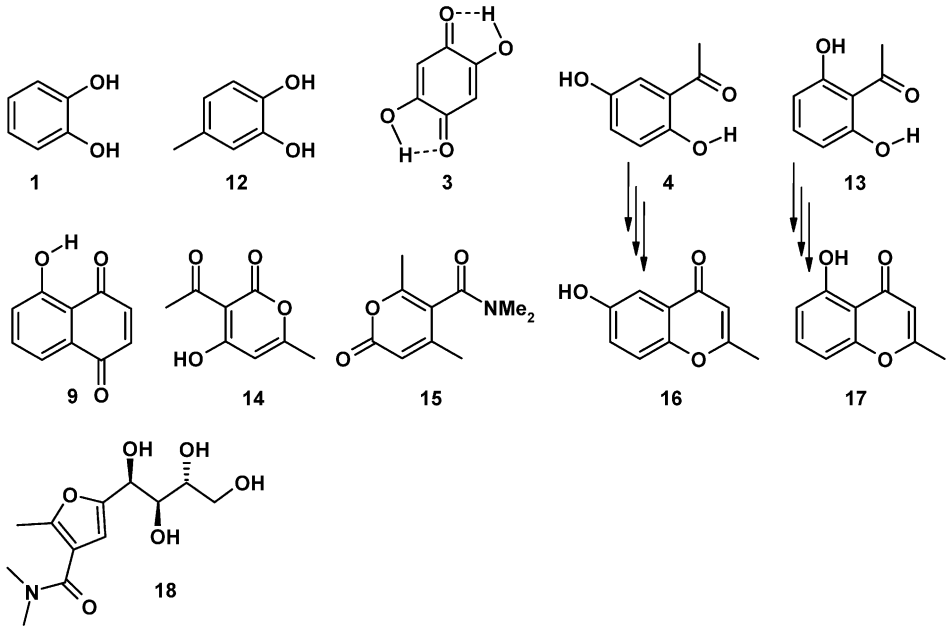

Fig. 3. Chromophores isolated from cellulose after thermal treatment in refluxing DMAc.

medium. As in the case of the other cellulose materials, also in this case the compounds causing the yellowish overall appearance could either be covalently linked to the high-molecular weight polymer structure, or simply be adsorbed to or included in the polymer matrix. The extraction procedure afforded six chromophores, as shown in Fig. 4. Identification was once more accomplished by NMR, MS, and comparison with authentic samples. The $BF_3 \cdot 2HOAc$-method was thus well suited to release chromophores also from cellulose triacetates.

Dehydroacetic acid (**14**) is a typical self-condensation product of acetic acid derivatives, which is formed via acetoacetic acid derivatives, see also Fig. 3. Compounds **3**, **12** and **13** are once more typical condensation products, generated from cellulose under the thermal or acidic conditions of acetate manufacture. Interestingly, all of these three compounds have been reported as aromatic condensation products of both hexoses and pentoses, so that from the structure of the chromophores neither cellulose (hexoses) nor xylan impurities (pentoses) can be unambiguously determined as the source. Compound **17** is a condensation product of **13** with acetic acid, formed during preparation of the acetate. It thus represents a secondary chromophore, which was formed from a primary carbohydrate condensation product. Furan **19** is formed by condensation of acetoacetic acid with the cellulose degradation product glucose in an aldolization–condensation sequence. It is distinguished from furan **18** just by the presence of the free carboxyl function instead of the *N*,*N*-dimethylamide group. While **18** was completely released into the reaction medium, but did not remain bound to the cellulose matrix (Section 3.2.2), **19** was bound to the polymer (likely in covalent manner as an ester), and was released only by the extraction treatment.

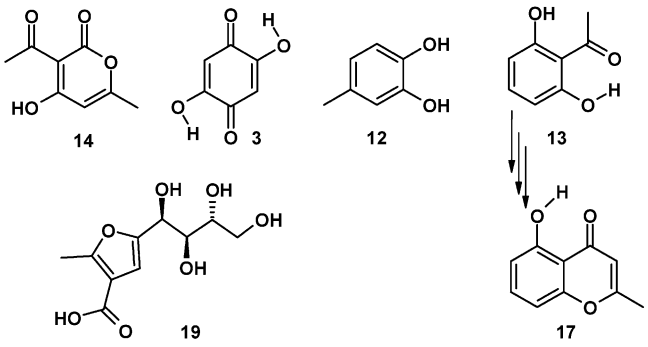

Fig. 4. Chromophores isolated from cellulose triacetate.

3.2.4. CCOA-labeled cellulose: probing the efficiency of the chromophore isolation method

The fluorescent label 'CCOA' (carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)-ethoxy]-amide, **20**) has been developed in response to a lack of accurate methods for the determination of carbonyl groups in cellulosic pulps and other higher-molecular weight carbohydrates [12]. It attaches selectively to the minute amounts of carbonyl structures, which are present in cellulosic pulps either as reducing end groups or as oxidized spots along the polymer chain. After dissolution in DMAc/LiCl and gel permeation chromatographic analysis with multiple detectors, the validated labeling procedure [13] provides the traditional molecular weight (MW) distribution, the overall carbonyl content as a sum parameter, and the MW-dependent carbonyl profiles of the respective cellulose sample. The carbonyl content of common cellulosic pulps ranges usually between 10 and 40 μmol g^{-1} [12].

To check the efficiency and accuracy of the chromophore

isolation method we applied the procedure to a CCOA-labeled beech sulfite pulp with a thoroughly determined carbonyl content of 24 μmol g^{-1}. The fluorescent label was expected to be the major—if not the only—chromophore isolated, since the pulp was not supposed to contain other chromophoric substances. Furthermore, the amount of label released should at least roughly correspond to the value of 24 μmol g^{-1} determined by fluorescence/chromatography. Indeed, *N*-acetylcarbazol (**21**) was isolated as the chromophore derived from CCOA (Fig. 5), and its concentration—relative to the pulp—was determined to be 18.6 μmol g^{-1} [14], which can be considered a satisfying agreement, taking into account the complexity of the multi-step isolation–separation–purification sequence used. This result clearly advocates in favor of the new chromophore isolation method as being quite effective and accurate. It moreover offers a means to estimate the carbonyl content of those higher-molecular weight pulps, which are insoluble in DMAc/LiCl and were thus not analyzable according to the CCOA method so far.

4. Conclusions

No analytical approaches existed to date for the isolation and identification of chromophores on cellulosic fibers and other cellulosic materials. A novel isolation method has been developed, which applies boron trifluoride–acetic acid complex in combination with sodium sulfite for that purpose. The isolation procedure cleaves possible covalent links between aromatic chromophores and the fiber matrix, and converts most quinoid compounds into the corresponding aromatics beforehand.

For the first time, genuine chromophoric compounds were isolated from Lyocell material, from pulp after thermal treatment in DMAc and from cellulose triacetate. The chromophoric nature of the compounds in these three materials was strong enough to cause a visible yellowing, although their concentration was extremely low in the ppm range.

From the structure of the isolated compounds it was evident that some of the chromophores are (thermal, acidic or basic) condensation products of (mono)saccharides, which in turn come from cellulose degradation. These primary chromophores—mainly 2,5-dihydroxybenzoquinone, polyphenols, and hydroxyacetophenones—were found in all cellulosic materials investigated. Also chromophores coming solely from condensation reactions of the solvent or reaction medium (NMMO, DMAc, or acetic acid, respectively) without participation of the cellulose component were found. The primary chromophores can undergo further condensation processes, which might also involve solvents or other coreactants present. Mainly polycyclic compounds of aromatic and quinoid nature (naphthoquinones, chromanones) are formed this way. Thus, in the cases investigated, the color generation can by no means be seen as a mere consequence of condensation reactions of cellulose degradation products, but it must be regarded instead as a complex set of reactions between carbohydrate degradation and condensation products, the respective reaction medium, and degradation products of this medium.

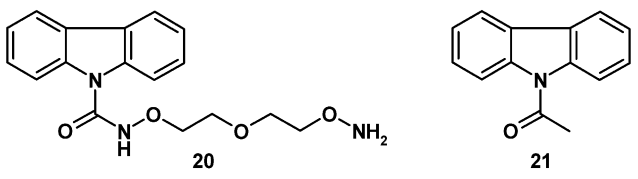

Fig. 5. Chromophore **21** isolated from pulp labeled with CCOA (**20**).

Application of the chromophore isolation method to a CCOA-labeled pulp containing an exactly known amount of the fluorescent CCOA label demonstrated the efficiency of the method in releasing aromatic structures from the pulp. The approach may also open new ways in the analysis of residual lignins or in monitoring bleaching efficiencies. In general, knowledge of the structure of the chromophoric compounds in cellulosics is supposed to help devise possible means for their temporary or permanent removal, which is a topic of further studies in our lab.

Acknowledgements

The authors are grateful to Mr Andreas Pitschmann and Mr Peter Schmid, University of Natural Resources and Applied Life Sciences, for practical assistance. The financial support by the Lenzing AG, Austria, is gratefully acknowledged.

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[13] See Refs. [3] and [12].
[14] The value was determined gravimetrically and by ^{1}H NMR measurements using internal standards.