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Singlet oxygen degradation of lignin: a GC–MS study on the residual products of the singlet oxygen degradation of a steam exploded lignin from beech

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Abstract

The steam exploded lignin from beech obtained with log $R_0 = 3.42$ was characterized by using elemental analysis, UV, and NMR spectroscopy. The irradiation of this lignin in acetonitrile–ethanol 1 : 1 in the presence of both oxygen and Rose Bengal gave a residue that was chromatographed on silica gel and then analyzed through GC–MS. The analysis of the fractions showed the presence in the residue of small molecules deriving from lignin such as vanilline and sinapyl alcohol. Furthermore, palmitic acid and 2,5-dimethoxyhydroquinone were detected. Finally, some phenylalkanes, mainly deriving from tridecane, were detected in the last fraction deriving from the column chromatography.

Keywords: Singlet oxygen; GC–MS; Lignin

1. Introduction

The presence of singlet oxygen in light-induced yellowing of wood containing paper was supposed several years ago [1]. Nimz showed that several monomer and dimer models of lignin can interact with singlet oxygen [2]. Subsequently, Forsskåhl showed that excited lignin was able to sensitise singlet oxygen [3]. Recently, we found that some lignin models and lignins from steam explosion can undergo several modifications when irradiated in the presence of both oxygen and Rose Bengal [4–6]. In particular, we could see that most of the employed model compounds gave a β-C–O cleavage reaction. This type of reaction was described as occurring by using direct irradiation of lignin models with UV light at λ 300–350 nm [7–14]. This reaction occurs also in the absence of carbonyl groups in the molecule and, when the number of the substituents on the phenoxy part of the molecule decreases the reactivity of the models towards singlet oxygen, cleavage of the phenoxy part of the molecule was observed [5]. Furthermore, the treatment of lignins from steam explosion with singlet oxygen led to a clear degradation of the lignins as showed by gpc chromatograms and UV analyses [6]. Recently, we showed that singlet oxygen can be used to induce degradation of both Klason lignin and lignin in steam exploded pulp [15,16].

In this paper, we want to report our results on the analysis of the residue of the singlet oxygen degradation of a steam exploded lignin from beech. In fact, in order to estimate the potential utility of this method in the delignification of pulp the analysis of the residue to be treated can be an important datum. Furthermore, we want to estimate the possibility of the use of photochemical degradation of lignin as a method to obtain fine chemicals from lignin.

2. Materials and methods

The material used as source of lignin (beech) was mechanically reduced in pieces of about 1 cm of length and added with water to rise its initial content to the value of 50%. Steam explosion runs were carried in a 10 l batch reactor, loading about 0.5 Kg of material each cycle. Treatment conditions were 188°C and 3 min with log $R_0 = 3.42$. The raw material (100 g) was extracted two times with hot water (250–300 ml, 65 ± 5°C) in order to eliminate sugars and hemicelluloses. The extraction of lignin from exploded materials has been carried out by 1.5% sodium hydroxide solution (250 ml) at 90°C in 15 min for two times. Lignin was precipitated at pH 2 with 20% H_2SO_4 when the solution was still warm, filtered, washed, and dried at 105°C.

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Elemental analyses were obtained with a Carlo Erba Elemental Analyzer 1106. ^{13}C NMR spectra were recorded with a Bruker 300 AM instrument. All the spectra were recorded in DMSO-d_6. Gel permeation chromatography analyses were performed on a Varian HPLC by using H-P Plgel 5 μ column. The lignin samples were acetylated (acetic anhydride and pyridine) before the use. THF was used as mobile phase. Spectrophotometric grade THF was used and distilled (oven $LiAlH_4$) before the use. The chromatograms were obtained using an UV detector at 280 nm. The conversion from elution time to molecular weight was performed by using a calibration obtained by using polystyrene samples [17]. Cary 2300 spectrophotometer was used for the UV spectra. Spectrophotometric grade DMF was used as solvent. In same cases the 1:1 mixture CH_3CN–EtOH was used as solvent.

2.1. Reactions with singlet oxygen

A solution of the lignin (10 mg) in a 1 : 1 mixture of acetonitrile–ethanol (10 ml) containing 5×10^{-4} M Rose Bengal was irradiated in a Pyrex tube surrounded by a Pyrex water-jacket connected to a Haake D9-G thermostat to maintain the temperature at 13.0 + 0.1°C. The Pyrex tube was dipped into a 1% (w/v) solution of $NaNO_2$ in order to cut-off the irradiation at 400 nm. The solution was previous saturated with bubbling oxygen for 1 h. The irradiation was performed by using a 50 W tungsten-halogen lamp. The solvent was evaporated and the residue was chromatographed on silica gel eluting with 3 : 7 MeOH–$CHCl_3$. The collected fractions were analyzed through GC–MS. Mass spectra were obtained with a Hewlett-Packard 5971 mass-selective detector on a Hewlett-Packard 5890 gas chromatograph [OV-1 capillary column between 70 and 250°C (20°C min^{-1})].

3. Characterization of lignins from steam explosion

The results of elemental analyses were: C, 51.53% and H, 5.04%. We analysed the presence of carbon and hydrogen in order to characterize the lignin, but also the presence of both nitrogen as a marker of the presence of proteic materials in the lignin and sulphur as a marker of the presence of sulphonated lignins. The presence of sulphur in our samples was not detected. The elemental analysis allows us to give a molecular formula expressed in phenylpropanoid (C9) units of $C_9H_{10.57}O_{5.69}$ corresponding to the molecular weight of 210.

The distribution of acetylated lignins considering their molecular weights was obtained by using gel permeation chromatography. The results are depicted in the Fig. 1. Most of the molecules of our sample show a molecular distribution in the range 100–100,000.

The UV spectra of our samples were recorded in DMF. We recorded also the differential spectra obtained carrying out the spectrum of the samples in 1 M NaOH versus the standard solution in DMF. These data allow us to give the amount in mEq g^{-1} of some structural features in the lignin samples. In this case, we was able to give the amounts of syringyl and guaiacyl phenols (Type I), the amounts of phenols containing conjugated double bonds (i.e. HO–Ar–CH=CH–CH_2OH, Type II), and the amounts of stilbenic phenols (Type IV) [18]. In this case, our lignin showed absorptions at $\lambda = 277$ nm ($D = 15.60$ l g^{-1} cm^{-1}), $\lambda = 308$ nm ($D = 9.20$ l g^{-1} cm^{-1}), and at $\lambda = 340$ nm ($D = 5.80$ l g^{-1} cm^{-1}).

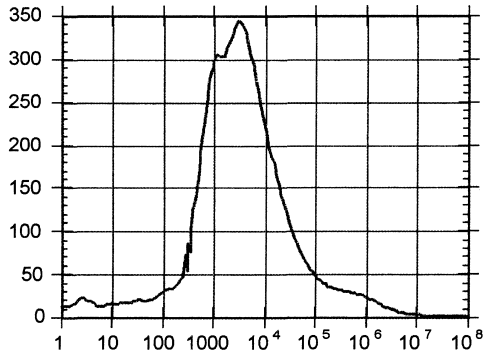

Fig. 1. MW distribution of lignin from beech.

Finally, the characterization of the lignins used in this work was completed by using the ^{13}C NMR spectroscopy. With our sample, we observed signals at δ (DMSO-d_6) 152, 147.5, 138, 134.5, 115, 104.5, 86, 72, 59.5, 55.8 and 40 ppm [19,20]. From these data, we can observe the presence of guaiacyl and syringyl structures. These structures are both β-O-4 etherified and non-etherified. We observe the presence of both threo and erithreo structures. We note the presence of structures of type cinnamaldehyde and stilbenes. The ^1H NMR spectrum of acetylated sample of lignin in $CDCI_3$ showed signals at δ 1.22, 2, 2.3, 3.7, 4.27, 4.4, 4.5, 6, and 6.5–7 ppm.

4. Analysis of the residual lignin

The residue of the treatment of lignin with singlet oxygen was chromatographed on silica gel eluting with methanol–chloroform mixtures. We collected some fractions. The chromatogram of the first fraction is represented in Fig. 2.

The peak at the retention time 5.54 min can be identified as $CH_3COCH_2OCH_2CH_2CH_3$: in fact, it showed a peak in the MS spectrum at *m/z* 116 with fragmentation at *m/z* 74 ($CH_3COCH_2O^+$), 58 ($CH_3COCH_2^+$), 46, 44 ($CH_3CO^+ + H^+$), and 43, in agreement with the proposed structure. The peak at rt 5.80 min was identified as $CH_3COCH_2OCOOCH_2CH_2CH{=}CH_2$: in fact its MS spectrum showed a peak at *m/z* 156, and fragments at *m/z* 102 ($CH_3COCH_2OCO^+$), 74 ($CH_3COCH_2O^+$), 46, 44 ($CH_3CO^+ + H^+$), and 43, in agreement with the proposed structure. The peak at 8.31 min is vanilline with molecular

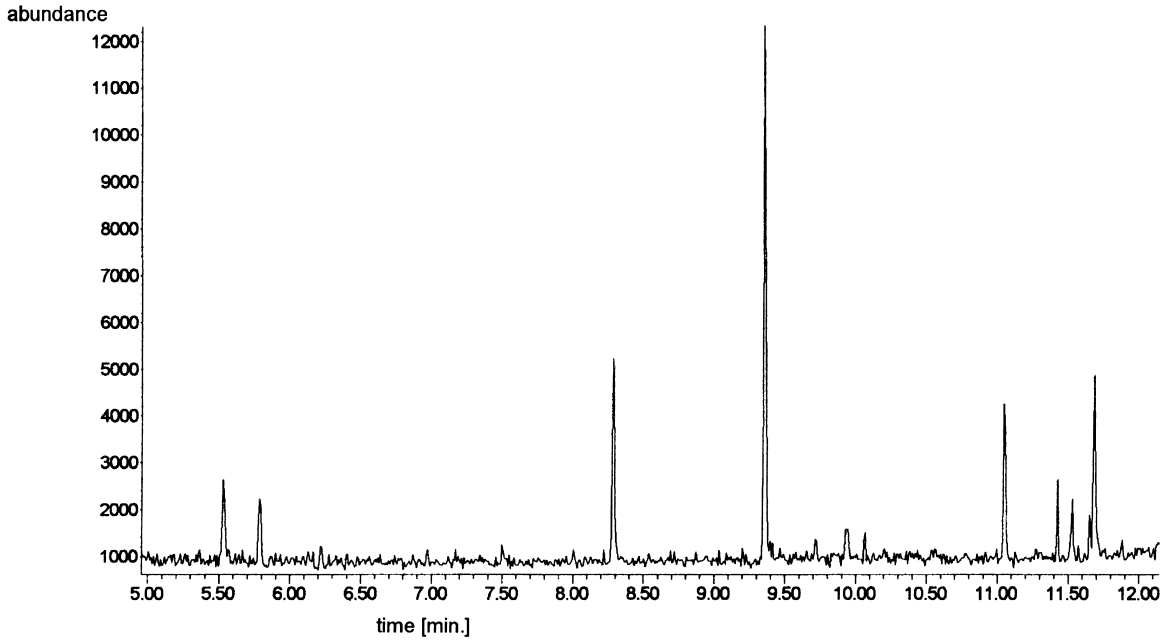

Fig. 2. GC chromatogram of fraction 1 of the chromatography of residual lignin after singlet oxygen treatment.

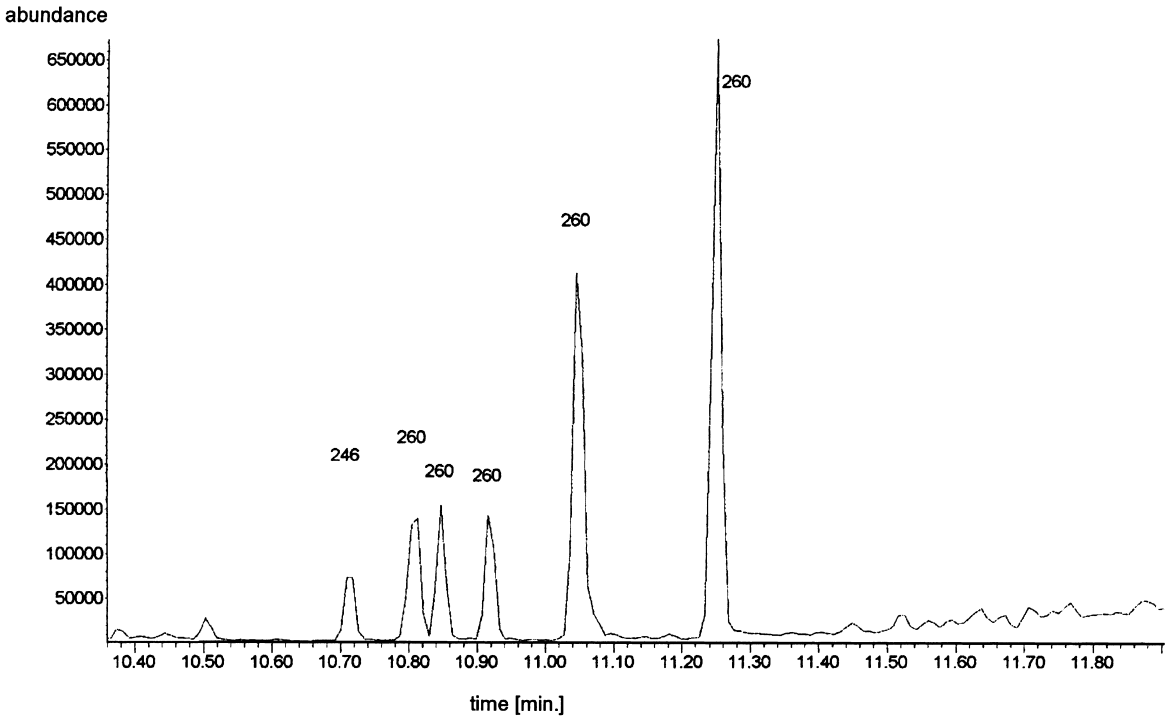

Fig. 3. GC chromatogram of fraction 5 of the chromatography of residual lignin after singlet oxygen treatment.

peak at *m*/*z* 152 in its MS spectrum. The most abundant peak in the chromatogram reported in Fig. 2 is that at 9.36 min. The identification of this compound showed some problems. In fact, it showed a peak in the MS spectrum at *m*/*z* 170 and a M-2 peak at *m*/*z* 168. Then it showed peaks at *m*/*z* 155, 138, 127, 112, 97, 80 and 69 (100%). The most probable identification of this peak is 2,5-dimethoxyhydroquinone. The peak at 11.43 min can be identified as palmitic acid: it showed characteristic peaks at *m*/*z* 256, 213, 129, 73 (100%), 60, and 57 [21]. The peak with retention time 11.68 min was identified as *trans*-3,5-dimethoxy-4-hydroxycynnamic alcohol (sinapyl alcohol): in fact, it showed a peak in the

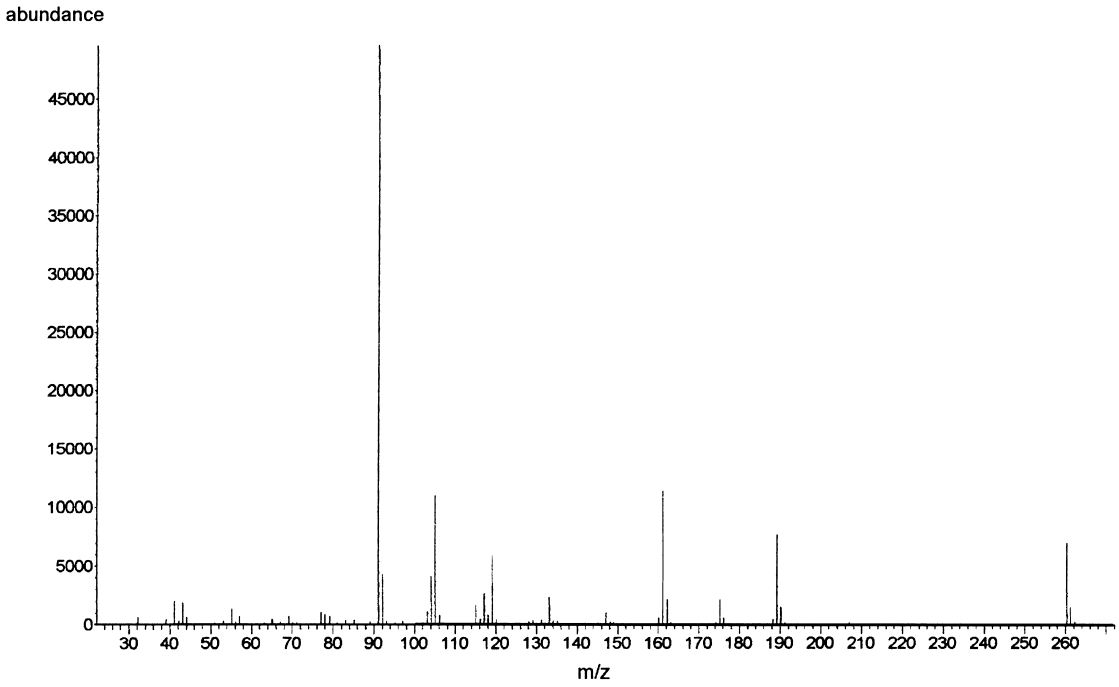

Fig. 4. MS spectrum of the peak at the retention time 10.81 min in Fig. 3: 6-phenyltridecane.

MS spectrum at *m*/*z* 210 (100%), and the fragmentation is identical to that reported for this compound in the literature [22].

The fractions 2–4 of the eluant did not show any relevant product, we observed the presence of traces of organic materials. The fifth fraction of the eluant showed some interesting peaks. The chromatogram of this fraction is reported in Fig. 3.

The first peak at retention time 10.72 min showed a MS spectrum with a parent ion at *m*/*z* 246. All the other peaks in Fig. 2 showed parent ion in the MS spectra at *m*/*z* 260. Its identification could be performed by comparison with the electronic library Wiley 6N and we obtained the following results: the peak at retention time 10.72 min was 2-phenyldodecane; the peak at retention time 10.81 min was identified as 6-phenyltridecane (Fig. 4); the peak at retention time 10.85 min was 5-phenyltridecane; the peak at retention time 10.92 min could be attributed to 4-phenyltridecane; furthermore, the peak at 11.04 min was assigned to 3-phenyltridecane, while the main peak on the GC chromatogram at retention time 11.25 min was 2-phenyltridecane.

In this fraction, we obtained only a mixture of phenylalkanes mainly related to tridecane. The presence of alkanes in GC–MS study of lignins has been reported [21]. However, the author reported the presence of C22–C30 *n*-alkanes.

In conclusion, a severe treatment of steam exploded lignin from beech with singlet oxygen leads to an extensive degradation of the lignin. The analysis of the residue showed the presence of some lignin derivatives, such as vanilline or sinapyl alcohol, the presence of high oxidated phenols. We showed also the presence of palmitic acid. Finally, we observed the formation of some phenylalkanes in the reaction mixture, never observed before.

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