

Fine chemicals from singlet-oxygen-mediated degradation of lignin — a GC/MS study at different irradiation times on a steam-exploded lignin

Giovanni Bentivenga^a, Carlo Bonini^b, Maurizio D'Auria^{b,*}, Adriano De Bona^a, Giacomo Mauriello^b

^a *ITIS A. Einstein, Via P. Lacava, Corleto Perticara, 85012 Potenza, Italy*

^b *Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy*

Received 3 February 2000; accepted 11 April 2000

Abstract

One-hour irradiation of steam exploded lignin in the presence of singlet oxygen gave products showing high molecular weights. The irradiation at different times gave sinapyl alcohol, 4-hydroxy-3,5-dimethoxybenzaldehyde, and 2,4-dioctylphenol. It is interesting to note the isolation of a dehydroabiatic acid derivative only after the treatment of lignin with singlet oxygen for 5 h. After 12 h irradiation of the same sample the presence of long chain hydrocarbons (octadecane), alkenes (1-octadecene) or alcohols (1-eicosanol) was detected. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lignin; Singlet oxygen; Irradiation

1. Introduction

Recently, we studied the interaction between lignin and singlet oxygen after the initial works of Nimz and Turznik [1] and Forsskähl [2]. In particular, 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 [3–5]. In particular, we could see that most of the employed model compounds gave a β -C–O cleavage reaction. This reaction occurs also in the absence of carbonyl groups in the molecule, and when the number of 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 [4]. 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 [5]. We showed that singlet oxygen can be used to induce degradation of both Klason lignin and lignin in steam exploded pulp [6,7]. Finally, we reported our results on the analysis of the residue of the singlet oxygen degradation of a steam exploded lignin from beech after 24 h irradiation [8]. The analysis of the chromatographic 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.

In this paper, we want to report our results on the analysis of the residue of singlet oxygen degradation of lignin performed using different irradiation times. In fact, we want to estimate the possibility of the use of photochemical degradation of lignin as a method to obtain fine chemicals from lignin. In the previous work [8], only small molecules were obtained showing low molecular weights. In this work, we want to verify the effect of the irradiation time on the molecular weight of residual compounds.

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 to its initial content to the value of 50%. Steam explosion runs were carried in a 101 batch reactor, loading about 0.5 kg of material in 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, $65\pm 5^\circ\text{C}$) 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.

* Corresponding author. Tel.: +39-971-202-240; fax: +39-971-202-223. E-mail address: dauria@unibas.it (M. D'Auria)

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 $5\ \mu\text{m}$ 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 [9]. Cary 2300 spectrophotometer was used for the UV spectra. Spectrophotometric grade DMF was used as solvent. In some cases the 1:1 mixture $\text{CH}_3\text{CN-EtOH}$ was used as solvent. The physical properties and the characterization of the lignin used are reported elsewhere [8].

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 $13.0 \pm 0.1^\circ\text{C}$. 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 previously 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 GC (OV-1 capillary column between 70 and 250°C ($20^\circ\text{C min}^{-1}$)).

3. Results and discussion

3.1. One-hour irradiation

The irradiation of a solution of a steam exploded lignin in 1:1 acetonitrile–ethanol in the presence of oxygen and Rose Bengal for 1 h gave, after evaporation of the solvent, a residue which was chromatographed on silica gel. This way, we obtained four fractions. The GC/MS analysis of these fractions gave the following results: fraction 1 showed four principal peaks. The first showed a retention time of 4.75 min and fragments at m/z 129 (20% relative abundance), 86 (100%), 57 (18%), 44 (65%), and 41 (18%). Its identification could be performed by comparison with the electronic library Wiley 6N: in this case the mass spectrum was identified as that of di-*n*-butylamine. It is not clear about the origin of this amine. Probably, it is only a residue of proteic materials. The other peak we could identify was that at retention time 12.68 min. The mass spectrum was very simple showing peaks at m/z 318 (5% relative abundance), 248 (24%), 247 (100%) 175 (9%), 161 (5%), 147 (3%), and 57 (13%). The comparison of this spectrum with the electronic library Wiley 6N identified the compound as 2,4-dioctylphenol.

The second fraction showed three peaks and two of them were identified. The first peak, the most abundant one on the chromatograms, showed a retention time of 12.34 min. It was identified as *trans*-3,5-dimethoxy-4-hydroxycinnamic alcohol (sinapyl alcohol); in fact, it showed a peak in the mass spectrum at m/z 210 (100%), and the fragmentation is

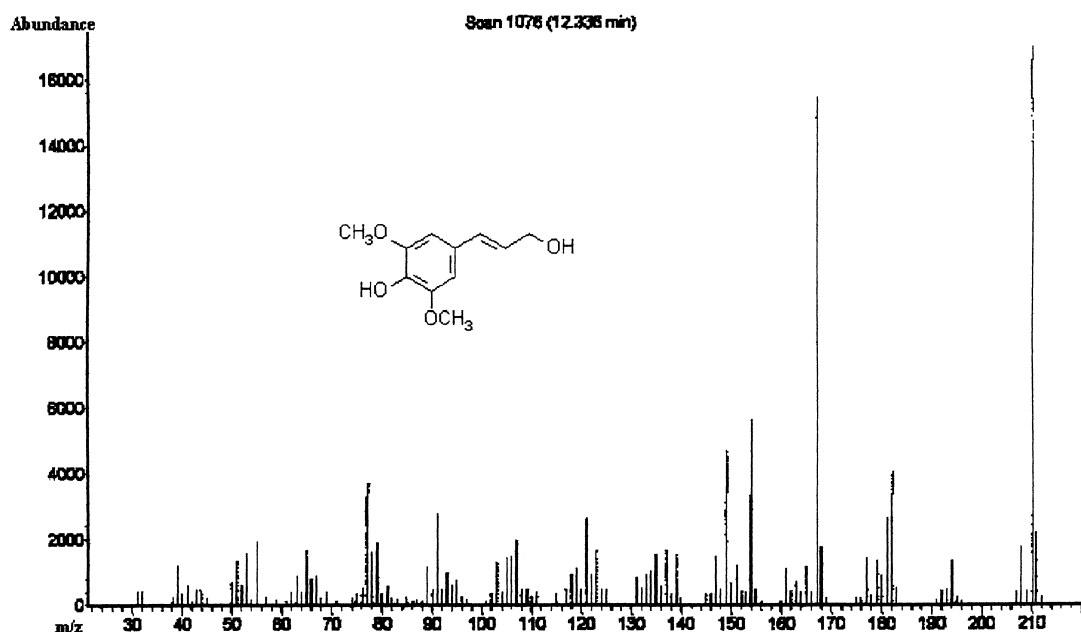


Fig. 1. MS spectrum of sinapyl alcohol.

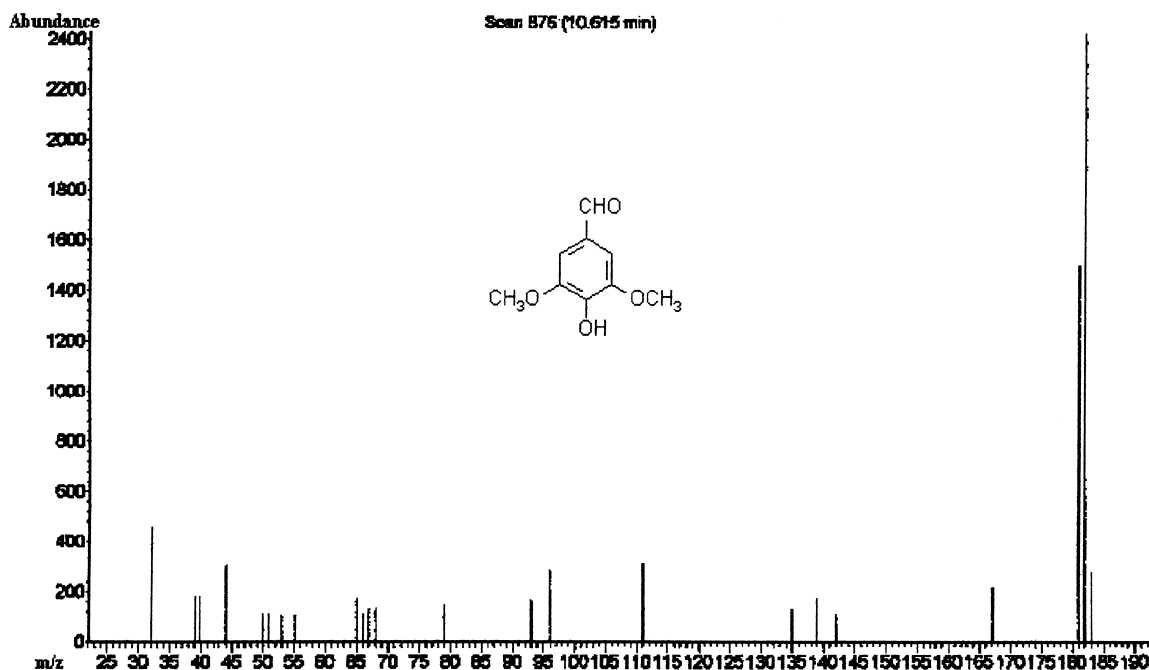


Fig. 2. MS spectrum of 4-hydroxy-3,5-dimethoxybenzaldehyde.

identical to that reported for this compound in the literature (Fig. 1) [10]. The second peak showed a retention time of 12.68 min and a mass spectrum identical to that identified as 2,4-dioctylphenol.

The third fraction showed a lot of peaks where we were able to identify only that at retention time (r.t.) 12.34 min (*trans*-3,5-dimethoxy-4-hydroxycinnamic alcohol) and the most abundant one at r.t. 12.68 min (2,4-dioctylphenol).

The fourth fraction showed only one peak with retention time 12.68 min, clearly identified as 2,4-dioctylphenol.

One-hour irradiation of lignin gave a lot of molecules. We were able to identify only three substances. Probably, the

other peaks observed in the chromatograms refer to products with molecular weight higher than the instrumental limit (m/z 600): in this case, we were able to detect only fragments.

3.2. Three-hour irradiation

The irradiation of the steam exploded lignin under the same conditions for 3 h and the subsequent column chromatography allowed us to obtain two fractions. The first fraction was mainly constituted by a compound that showed a retention time of 10.61 min. The mass spectrum showed a parent peak at m/z 182 (Fig. 2). It was identified as

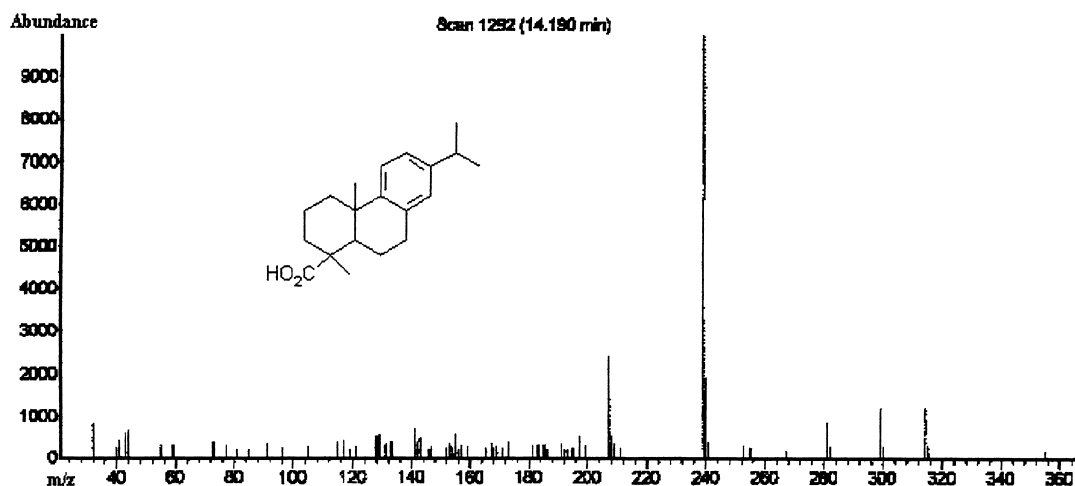


Fig. 3. MS spectrum of dehydroabietic acid methyl ester.

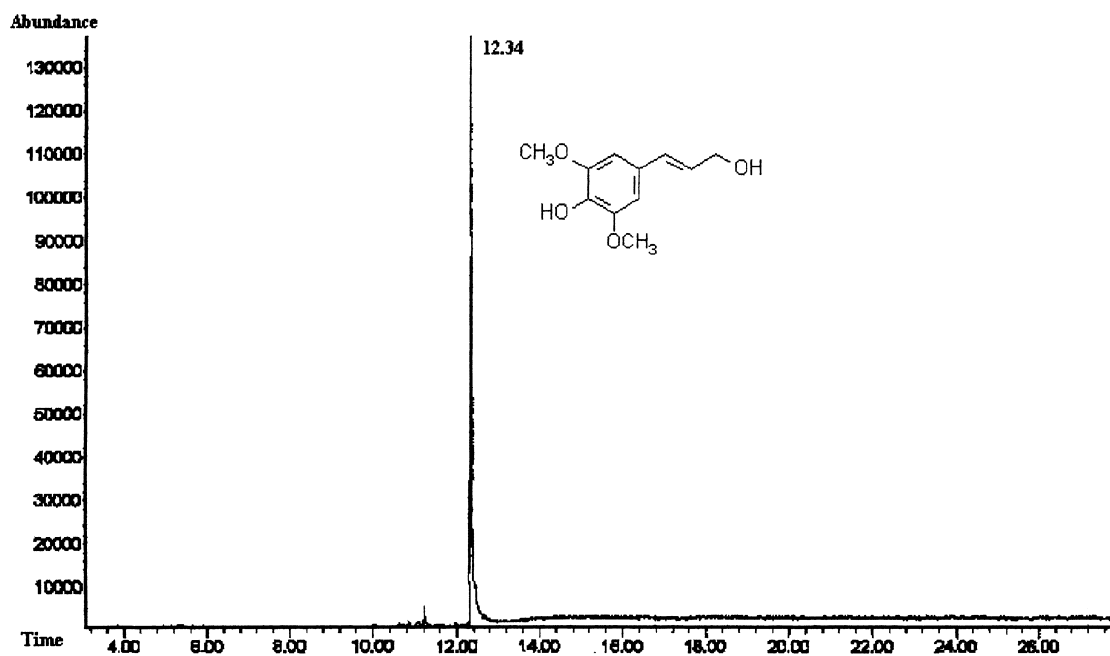


Fig. 4. Chromatogram of the fraction 4 obtained after 8 h irradiation of steam-exploded lignin from beech with singlet oxygen.

4-hydroxy-3,5-dimethoxybenzaldehyde. The second fraction contains only one peak whose mass spectrum was identical to that of sinapyl alcohol.

3.3. Five-hour irradiation

The treatment of the steam exploded lignin with oxygen and Rose Bengal for 5 h and the chromatography on silica gel gave four fractions. The fractions 1–3 showed one peak with a retention time of 14.20 min. Mass spectrum (Fig. 3) showed peaks at m/z 314, 299, and 239 (100%); comparison with electronic library Wiley 6N identified this compound as dehydroabietic acid methyl ester. In the fourth fraction, we found 2,4-dioctylphenol and methyl ester of dehydroabietic acid.

3.4. Eight-hour irradiation

Eight-hour irradiation of lignin in the presence of singlet oxygen gave three fractions. The first one contained 4-hydroxy-3,5-dimethoxybenzaldehyde and sinapyl alcohol. The other fractions contained only sinapyl alcohol (Fig. 4).

3.5. Twelve-hour irradiation

Finally, after 12 h irradiation column chromatography gave three fractions: the first contained 1-octadecene, octadecane, and 1-eicosanol, while the other fractions were constituted by sinapyl alcohol.

In conclusion, while 1 h irradiation of steam exploded lignin in the presence of singlet oxygen gave products show-

ing high molecular weights, the irradiation at different times gave sinapyl alcohol, 4-hydroxy-3,5-dimethoxybenzaldehyde, and 2,4-dioctylphenol. It is interesting to note the isolation of a dehydroabietic acid derivative only after the treatment of lignin with singlet oxygen for 5 h. Furthermore, it is not clear about the presence of long chain hydrocarbons (octadecane), alkenes (1-octadecene) or alcohols (1-eicosanol) only after 12 h irradiation of the same sample.

References

- [1] H.H. Nimz, G. Turznik, *Cellulose Chem. Technol.* 14 (1980) 727.
- [2] I. Forsskähl, *J. Photochem.* 25 (1984) 197.
- [3] C. Crestini, M. D'Auria, *J. Photochem. Photobiol. A: Chem.* 101 (1996) 69.
- [4] C. Crestini, M. D'Auria, *Tetrahedron* 53 (1997) 7877.
- [5] C. Bonini, M. D'Auria, L. D'Alessio, G. Mauriello, D. Tofani, D. Viggiano, F. Zimbardi, *J. Photochem. Photobiol. A: Chem.* 113 (1998) 119.
- [6] G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona, G. Mauriello, *Chemosphere* 39 (1999) 2409.
- [7] C. Bonini, M. D'Auria, G. Mauriello, D. Viggiano, F. Zimbardi, *J. Photochem. Photobiol. A: Chem.* 118 (1998) 107.
- [8] G. Bentivenga, C. Bonini, M. D'Auria, A. De Bona, *J. Photochem. Photobiol. A: Chem.* 128 (1999) 139.
- [9] G. Gellerstedt, Gel permeation chromatography, in: S.Y. Lin, C.W. Dence (Eds.), *Methods in Lignin Chemistry*, Springer, Berlin, 1992, p. 487.
- [10] D. Meier, O. Faix, Pyrolysis–gas chromatography–mass spectrometry, in: S.Y. Lin, C.W. Dence (Eds.), *Methods in Lignin Chemistry*, Springer, Berlin, 1992, p. 177.