

# Photochemical study of 4-(4,9-dimethoxy-2,11-*n*-dipropyl-6,7-dihydro-5,8-dioxa-dibenzo[a,c]cycloocten-6-yl)-2-methoxyphenol, a lignin model of phenolic dibenzodioxocin unit

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## Abstract

The photochemical behavior of compound **2** was studied as lignin model of phenolic dibenzodioxocin, due to the presence of photoreactive  $\alpha$ -O-4,  $\beta$ -O-4 linkages and phenolic group. The latter, very sensitive to oxidation, should increase the dibenzodioxocin photoreactivity compared to the non-phenolic dibenzodioxocin lignin model **1** ( $\Phi_R = 0.37$ ). Irradiation of **2** in non-degassed ethanol solutions at 285 nm gave colored solutions. The reaction was found to be inefficient ( $\Phi_R = 0.015$ ). Analysis of the photoproducts by mass spectrometry suggests that reversible formation of an intermediate quinone-methide, by  $\alpha$ -O-4 bond cleavage, might account for the low quantum yield value. The short wavelength fluorescence emission observed for compound **1**, compared to that of biphenylbiphenol **4**, was also found in molecule **2**, confirming the important role played by the dibenzodioxocin ring in the fluorescence emission of these structures.

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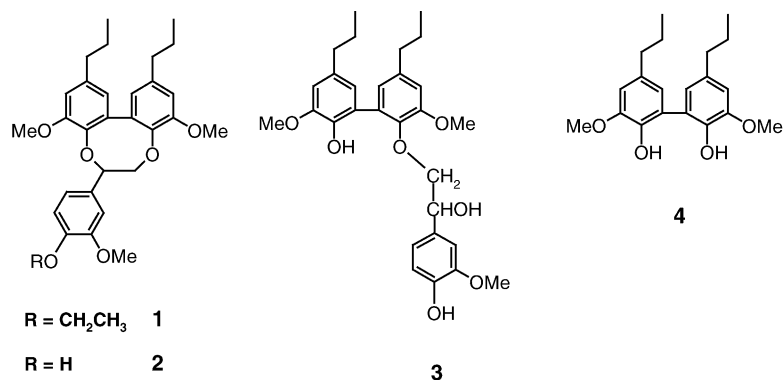
**Keywords:** Dibenzodioxocins; Lignin models; Fluorescence; Photoreactivity

## 1. Introduction

It is generally accepted that photodegradation of lignocelulosics is mainly due to photooxidation of lignin [1]. The main observation of this phenomenon is the photoyellowing of high-yield pulp and clear woods [2,3]. It has been shown that phenoxy radicals are key intermediates. They are formed through a variety of pathways: hydrogen abstraction of phenolic hydrogen by excited  $\alpha$ -carbonyl [4] or singlet oxygen [5], direct oxidation of phenols absorbing near-UV light [6], photocleavage of phenacyl-aryl ethers [7] and cleavage of the  $\beta$ -O-4 bond in arylglycerol- $\beta$ -aryl ethers [8]. Phenoxy radicals are oxidized in colored com-

pounds, such as *o*-benzoquinones, which are detected during the early stages of the photoyellowing [9]. Also the hydroquinone/benzoquinone redox systems were implicated in the coloration process of lignocelulosics [10–14]. Hydroquinones and catechols belong to phenol structures that absorb light between 300 and 400 nm in the lignocelulosics, and they are reactive units [11,12]. By contrast, coniferyl alcohol [15] and phenolic stilbenes [16,17], which belong to conjugated phenols, are not responsible for the photoyellowing of lignin-rich pulps. Recently Brunow's group showed that a large part of biphenyl structures in lignin were etherified by  $\alpha$  and  $\beta$  carbons of an other phenylpropane unit to give an eight-member ring, dibenzodioxocin [18–20]. This structure is an important element of the polymer network [20]; it is considered as main branching point in lignins. Dibenzodioxocins were also studied as structural units involved in

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Scheme 1. Formulae of compounds involved in the study.

chemical pulping and bleaching [21,22]. Very recently [23], we described a photochemical study of compound **1**, as model of non-phenolic dibenzodioxocin structure in lignin, because the presence of both photoreactive  $\alpha$ -O-4 [24] and  $\beta$ -O-4 [9] linkages in the molecule should bring a high sensitivity to UV-light. It was shown that the photochemical conversion of compound **1** was very efficient ( $\Phi_R = 0.37$ ), and analysis of the photoproducts indicated that the first step of the reaction started cleaving the  $\alpha$ -O-4 bond, followed either by  $\beta$ -O-4 cleavage or formation of rearranged products. The color observed after irradiation, was found to be due to condensation of biphenyl-oxidized products (quinone type). A mechanism was proposed, based on separation and identification of the photoproducts. Considering the reactivity of **1**, it might be concluded that non-phenolic dibenzodioxocins are important chromophores for the photodegradation of lignocellulosic materials.

The presence of a phenol substituent in dibenzodioxocin unit might induce photochemical formation of quinone-methide structure [25] and change the general photochemical behavior of dibenzodioxocins. We report herein a photochemical study of a phenolic dibenzodioxocin lignin model **2** (Scheme 1). Its photoreactivity in dilute solution, monitored by UV-vis absorption and fluorescence emission spectroscopies, was studied by reference to the phenolic biphenyl derivatives **3** and **4**. A number of products, obtained by irradiation of compound **2** in more concentrated solutions, were then identified.

## 2. Experimental

### 2.1. General

The syntheses of compounds **2–4** have been previously reported [23]. Materials and solvents of appropriate grade (for synthesis or for spectroscopy) were obtained from Aldrich and used without further purification. <sup>1</sup>H NMR spectra recorded for the quantum yield measurements were obtained using a Bruker AC300 Fourier transform spectrometer (solvent: CD<sub>3</sub>OD). UV/Vis spectra versus irradiation time were

recorded on a Shimadzu UV-2501PC spectrometer. Separation of photoproducts was obtained using analytical TLC (Fluka silica gel F<sub>254</sub>, thickness 0.2 mm and Macherey-Nagel ALUGRAM RP-18W/UV<sub>254</sub>, thickness 0.15 mm) and preparative TLC (Macherey-Nagel SIL G-200 UV<sub>254</sub>, thickness 2.00 mm).

Photoproducts were analyzed by mass spectrometry using a VG Micromass AutoSpec Q under electronic ionization (EI 70 eV) or liquid secondary ion mass spectrometry (LSIMS, Cs<sup>+</sup> beam energy: 35 keV, matrix: *m*-nitrobenzyl alcohol, NBA) and a Thermo Electron LCQ Advantage apparatus (ion trap) using electrospray ionization in positive (ESI+) or negative (ESI-) mode. With the ESI technique, ions can be selected and fragmented by collision induced dissociation (CID) into their daughter ions.

Fluorescence spectra were recorded with a Hitachi F4500 apparatus at room temperature ( $\approx 25^\circ\text{C}$ ). The slits on the excitation and emission beams were fixed at 2.5 nm. The emission spectra were corrected for instrumental response. The fluorescence quantum yields were determined using biphenylbiphenol **4**, as standard [23], concentrations being adjusted at about  $10^{-5}$  mol L<sup>-1</sup>.

### 2.2. UV-irradiations

The photodegradation of compounds **1–4** using analytical conditions (ethanol, concentration  $\approx 10^{-4}$  mol L<sup>-1</sup>), was monitored by UV-vis absorption spectroscopy or fluorescence emission, in a 10 mm quartz cell, at different times. The irradiations were performed at 285 nm, using the excitation part of the fluorimeter (slit fixed at 10 nm). The irradiation setup used for preparative condition is described in reference [23]. A solution of compound **2** (50 mg) in absolute non-degassed ethanol (50 mL) (concentration  $2.10^{-3}$  mol L<sup>-1</sup>) was irradiated for 3 h. After solvent removal under low pressure, the residue was diluted with methylene chloride and separated by column chromatography. A first fraction (40 mg) was obtained by elution with CH<sub>2</sub>Cl<sub>2</sub>/MeOH mixture (95/5 (v/v)) and a second one (15 mg) by elution with methanol. The second fraction corresponds to colored oligomeric material, already observed after irradiation of the non-phenolic

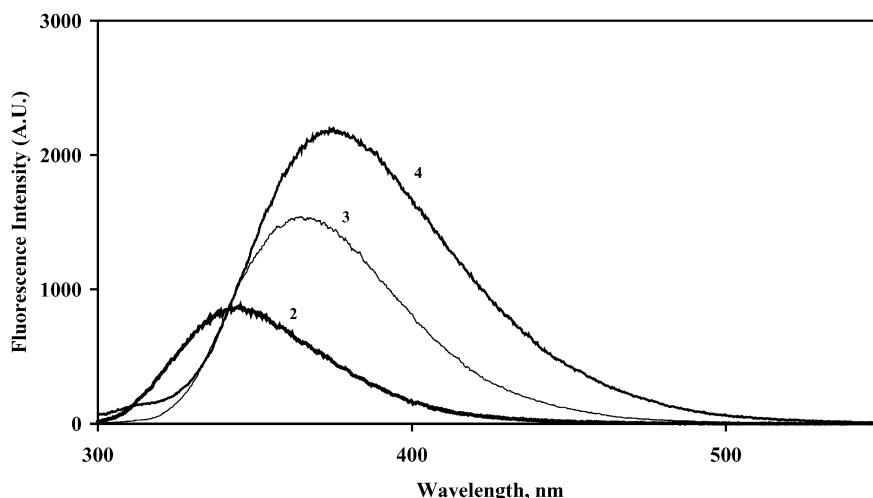


Fig. 1. Fluorescence emission spectra of biphenyl compounds **2**, **3** and **4** in non-degassed ethanol (concentration  $\approx 10^{-5}$  mol L $^{-1}$ ,  $\lambda_{\text{exc}}$ : 285 nm,  $f_{\text{exc}}$ : 2.5 nm,  $f_{\text{em}}$ : 2.5 nm, temperature  $\approx 25^\circ\text{C}$ ).

dibenzodioxocin **1** [23]. The first column fraction was separated in three parts by preparative TLC. Each fraction presents one single spot in analytical TLC (silica gel plates; diethyl ether/petroleum ether 6/4 (v/v)). The  $R_f$  and the weight of each part were respectively: 0.46 ( $\approx 10$  mg), 0.36 ( $\approx 20$  mg) and 0.26 ( $\approx 10$  mg). Attempt to use C $_{18}$  TLC plates for separation of the photoproducts was not conclusive, due to similar elution profile ( $R_f$ 's between 0.79 and 0.84, acetonitrile/H $_2$ O 9/1 (v/v)). The isolated photoproducts were extracted from silica gel using methanol, then the solutions were filtered with Millipore 13 mm Millex-LCR units (0.45  $\mu\text{m}$ ), before analysis by mass spectrometry.

The disappearance quantum yield of compound **2** in  $d_4$ -methanol solution was determined using a procedure described for compound **1** [23].

### 3. Results and discussion

#### 3.1. Fluorescence emission

In a previous study [23], we discussed the origin of the fluorescence of lignocellulosic materials, which remains quite controversial. Olmstead and Gray [26] proposed that fluorescence of lignocellulosics should be mainly due to cellulose, the lignin polymer acting as an inner filter. By contrast, Castellán's group proposed that structures such as biphenyl, coniferyl alcohol, phenylcoumarone and other stilbene elements (present in lignin polymer), should be responsible for the emission at about 400 nm [27–29], in accordance with Lundquist's studies [30]. It was found [23] that fluorescence emission of **1** was at shorter wavelength (345 nm) than the emission of the corresponding biphenylbiphenol **4** (380 nm). This observation was correlated with the conjugation between the phenyl rings of the biphenyl chromophore. It was concluded that dibenzodioxocins did not contribute

to the non-assigned long wavelength emission in lignins ( $>480$  nm).

The fluorescence emission spectra for compounds **2**, **3**, and **4** were comparatively measured in dilute ethanol solutions (Fig. 1) and their fluorescence quantum yields determined similarly as for compound **1** [23]. The fluorescence quantum yields and maximum emission wavelengths are reported in Table 1.

The molecular interpretation given for the non-phenolic dibenzodioxocin model **1** [23] (vide infra) applies to the phenolic derivative **2**. In comparison to biphenylbiphenol **4**, the behavior of compound **2** was similar to compound **1**: hypsochromic shift of the emission and decrease of the emission quantum yield. The emission quantum yield of compound **1** in non-degassed methanol was found to be 0.08, which is in the same order of magnitude than for compound **2**; this appears to be a characteristic of the dibenzodioxocin unit.

#### 3.2. Photochemistry

##### 3.2.1. Analytical conditions

It was previously reported that some lignin models, in dilute solution under UV irradiation, gave yellow compounds [31], including the non-phenolic dibenzodioxocin model **1** [23]. It was generally observed that the phenolic models were the most sensitive [6]. The absorption and fluorescence spectra of compounds **2**, **3** and **4**, irradiated at 285 nm in dilute

Table 1  
Fluorescence quantum yields of biphenyl compounds **2**, **3** and **4** in non-degassed ethanol (concentration  $\approx 10^{-5}$  mol L $^{-1}$ ) and wavelength of maximum fluorescence emission

Biphenyl compounds	$\phi_F$	$\lambda_{\text{max em}}$ (nm)
<b>2</b>	0.053	345
<b>3</b>	0.205	365
<b>4</b>	0.27	375

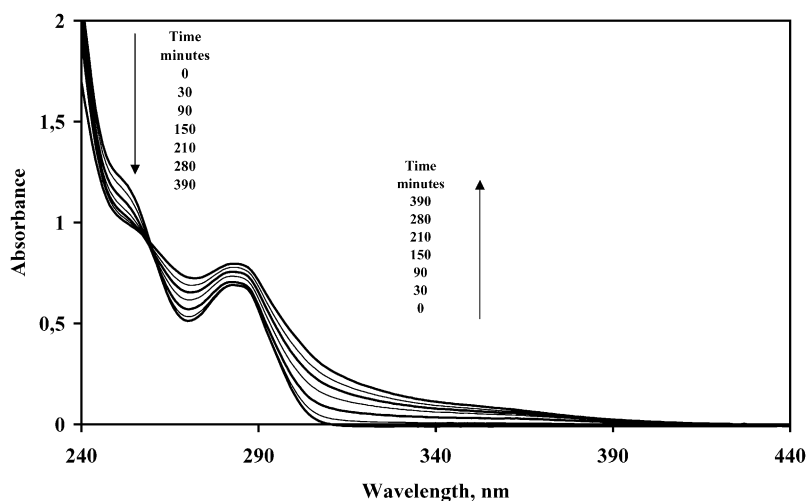


Fig. 2. Absorption spectra of compound **2** after irradiation at 285 nm in non-degassed ethanol solution (concentration  $\approx 10^{-4}$  mol L $^{-1}$ , path length: 1 cm, temperature  $\approx 25$  °C) for 0, 30, 90, 150, 210, 280 and 390 min.

non-degassed ethanol ( $\approx 10^{-4}$  mol L $^{-1}$ ) (see Section 2) have been recorded for various irradiation periods. Ethanol was selected to mimic carbohydrate fibers. The solutions were non-degassed, because the presence of an easily oxidizable phenolic group in compound **2** might increase its reactivity by comparison to the non-phenolic compound **1**. The UV/Vis absorption curves of irradiated compound **1** were not greatly changed by degassing the solutions. The absorption spectra of compounds **2**, **3** and **4**, in non-degassed ethanol, after irradiation at 285 nm for different periods of time, are presented in Figs. 2–4.

Comparison of Figs. 2–4 indicates that the photoreactivity is in the order: phenolic dibenzodioxocin **2** > biphenyl with  $\beta$ -O-4 element **3** > tetramethoxybiphenyl **4**, the latter being almost non-reactive. Disappearance quantum yield of phenolic dibenzodioxocin **2** in  $d_4$ -methanol was measured to be 0.015, indicating a low photochemical efficiency. This value is very different from the one measured for the non-

phenolic model **1** (0.37 in  $d_6$ -benzene). The high reactive quantum yield of compound **1** was explained by an efficient  $\alpha$ -O-4 bond cleavage in the first step of the photochemical process, followed by  $\beta$ -O-4 bond cleavage. The presence of a phenolic group in the dibenzodioxocin molecule adds competitive deactivation pathways to photoreactive states. The lower fluorescence quantum yield, observed for compound **2** (0.053) by reference to compound **1** (0.08 in non-degassed methanol), supports this hypothesis.

The fluorescence spectra evolution of irradiated solutions of compound **4** (Fig. 5) is in accordance with the low reactivity of the compound. Some quinonoid derivatives, which are formed by irradiation, might quench the biphenyl fluorescence and decrease the fluorescence intensity [32]. Fig. 6 shows that the fluorescence intensity decrease is more important for compound **3**; oxidation of the benzylic alcohol part, giving  $\alpha$ -carbonyl  $\beta$ -O-4 structural element, might increase the quenching of the phenolic biphenyl fluorescence.

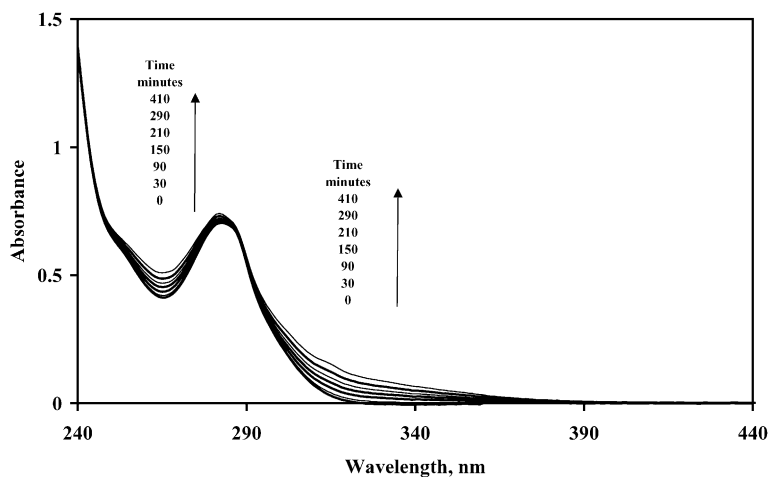


Fig. 3. Absorption spectra of compound **3** after irradiation at 285 nm in non-degassed ethanol solution (concentration  $\approx 10^{-4}$  mol L $^{-1}$ , path length: 1 cm, temperature  $\approx 25$  °C) for 0, 30, 90, 150, 210, 290 and 410 min.

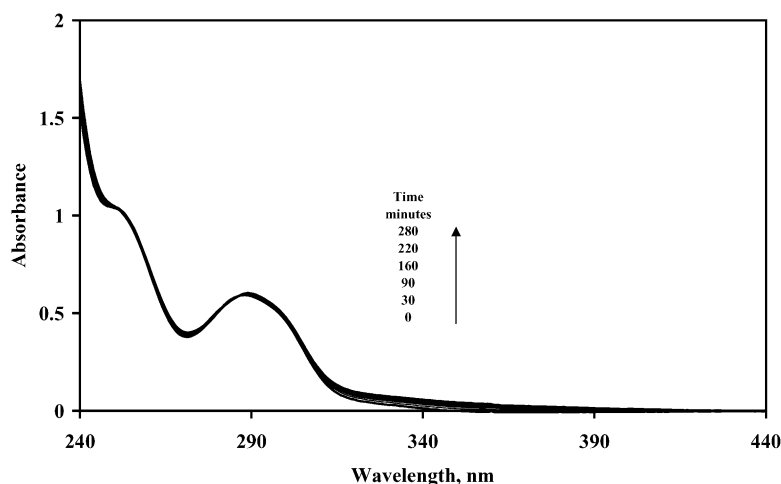


Fig. 4. Absorption spectra of compound **4** after irradiation at 285 nm in non-degassed ethanol solution (concentration  $\approx 10^{-4}$  mol L $^{-1}$ , path length: 1 cm, temperature  $\approx 25$  °C) for 0, 90, 150, 210, and 280 min.

The curves in Fig. 7 display a rapid decrease of the fluorescence intensity, followed by a bathochromic shift of the wavelength maxima to 360 nm. This value is indicative of the formation of a monophenolic biphenyl structural element such as molecule **3**. This will be confirmed by structural determination of some photoproducts.

### 3.2.2. Preparative conditions

The preparative conditions are described in the experimental section. The three fractions obtained by preparative thin layer chromatography (TLC) were analyzed by mass spectrometry. The first fraction ( $R_f = 0.46$ ) is composed of one major product and minute amounts of compounds **2** and **4**. Analysis of the product by high-resolution liquid secondary ion mass spectrometry (HRLSIMS) reveals a peak at 539.26628 amu (relative intensity, 38%), corresponding to  $(M + H)^+$  ion and to the formula C<sub>31</sub>H<sub>39</sub>O<sub>8</sub> (−3.3 ppm). The base peak at 341.17560, is consistent with the formula

C<sub>21</sub>H<sub>25</sub>O<sub>4</sub> (−0.9 ppm). The low resolution mass spectrum of the photoproduct, using electronic ionization (EI) and direct introduction, displays main peaks at  $m/z$ : 538 ( $M^+$ , 20%), 329 (88%) and 209 (100%). It can be observed that the sum of the  $m/z$  values 329 (C<sub>19</sub>H<sub>21</sub>O<sub>5</sub>) and 209 (C<sub>12</sub>H<sub>17</sub>O<sub>3</sub>) gives the molecular mass of the product. Its positive electrospray ionization mass spectrum ESI(+) shows two main peaks at  $m/z$  1099 and 561 attributed, respectively, to the cationized ions  $(M + M + Na)^+$  and  $(M + Na)^+$ ;  $M$  is the molecular fragment with a mass of 538 Da. Collision induced dissociation (CID) analysis of the ion at  $m/z$  561 leads to two main fragments at  $m/z$  352 and 209; the former corresponds to  $(m/z$  329 + Na) $^+$ . The same fragments were already obtained by EI mass analysis of the product (vide infra). Its ESI(−) mass spectrum implies direct loss of 46 amu, corresponding to the presence of an ethanol group in the molecule. All the mass spectrometry data obtained for the product are in accordance with structure **6** (Fig. 8). It is assumed that the hydroxyethyl

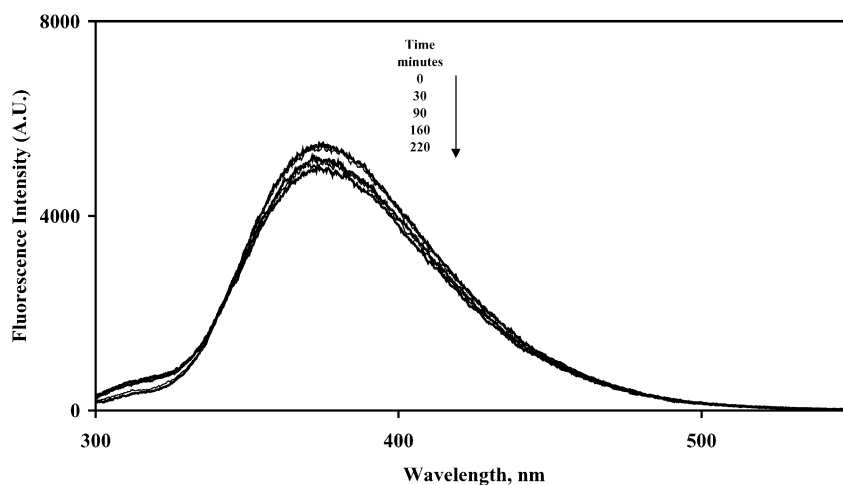


Fig. 5. Fluorescence spectra of compound **4** after irradiation at 285 nm in non-degassed ethanol solution (concentration  $\approx 10^{-5}$  mol L $^{-1}$ ,  $\lambda_{exc}$ : 285 nm,  $f_{exc}$ : 2.5 nm,  $f_{em}$ : 2.5 nm, temperature  $\approx 25$  °C) for 0, 30, 90, 160 and 220 min.

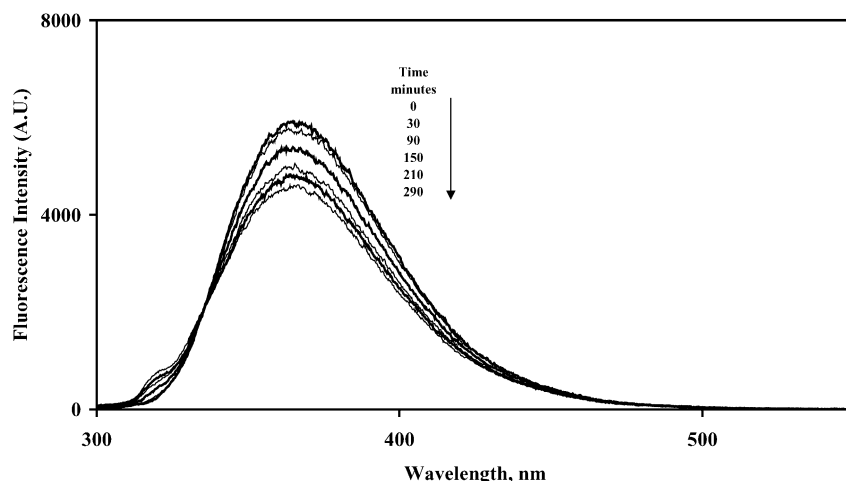


Fig. 6. Fluorescence spectra of compound **3** after irradiation at 285 nm in non-degassed ethanol solution (concentration  $\approx 10^{-5}$  mol L $^{-1}$ ,  $\lambda_{\text{exc}}$ : 285 nm,  $f_{\text{exc}}$ : 2.5 nm,  $f_{\text{em}}$ : 2.5 nm, temperature  $\approx 25$  °C) for 0, 30, 90, 150, 210 and 290 min.

fragment is substituted at carbon number 1, instead of carbon number 2. It corresponds to the most stable radical formed from ethanol by hydrogen abstraction.

The second fraction ( $R_f = 0.36$ ) consists of the starting phenolic dibenzodioxocin **2**. It displays the same low resolution EI mass spectrum (molecular peak  $m/z$  478 (100%)) as an authentic dibenzodioxocin **2** sample.

Analysis of the third fraction ( $R_f = 0.26$ ) by mass spectrometry indicates that it is essentially composed of compound **4** and minute amounts of other products. This fraction displays similar low resolution EI mass spectrum (molecular peak  $m/z$  330) as an authentic biphenylbiphenol **4** sample. The same conclusion is obtained from ESI mass analysis.

A special attention was given to the mass spectrum of the phenolic dibenzodioxocin **2** because the fragmentation pattern observed by EI mass spectrometry very often involves similar mechanisms than those found after photochemical excitation. The HREI mass spectrometry analyses of com-

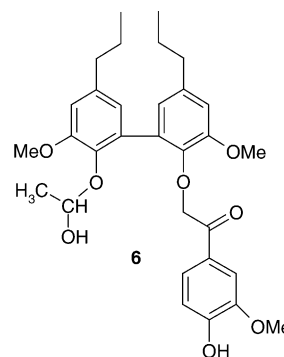


Fig. 8. Structure of compound **6** identified by mass spectrometry.

pound **2** led to a molecular mass of 478.23561 instead of 478.23554 (−0.2 ppm), for C<sub>29</sub>H<sub>34</sub>O<sub>6</sub>. Two smaller peaks were observed at  $m/z$  341 (34%) and 299 (22%). The exact mass of  $m/z$  341 (341.17534) is in good agreement with

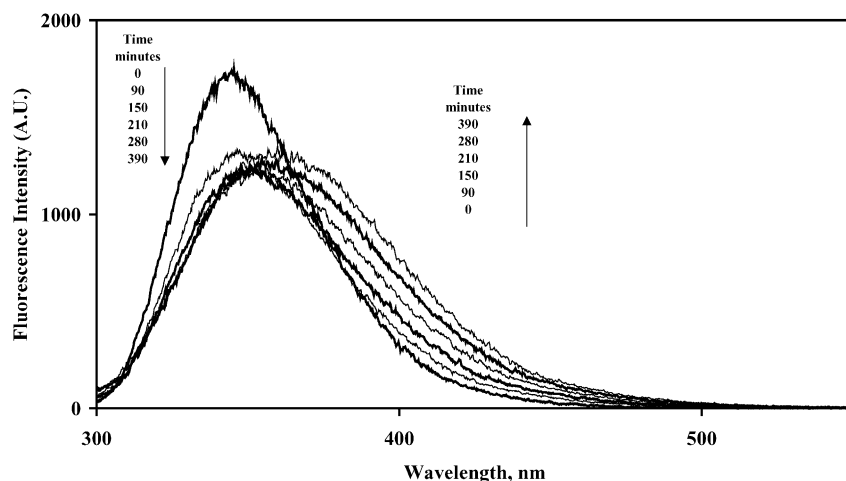
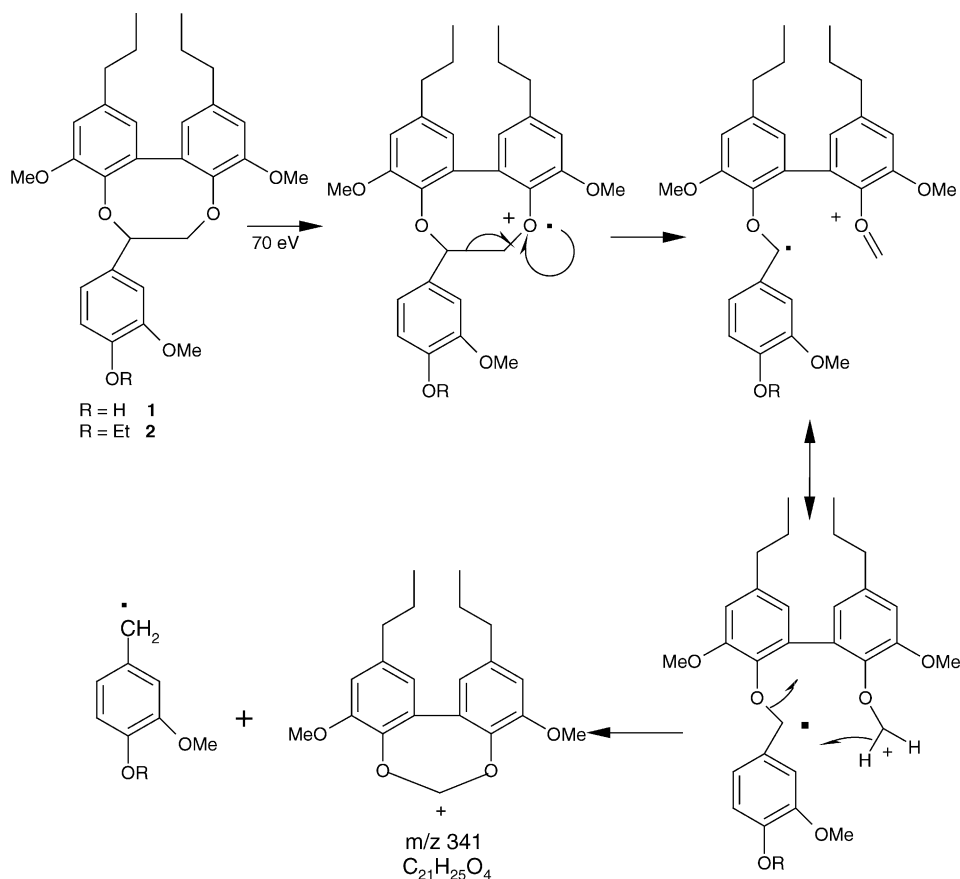


Fig. 7. Fluorescence spectra of compound **2** after irradiation at 285 nm in non-degassed ethanol solution (concentration  $\approx 10^{-5}$  mol L $^{-1}$ ,  $\lambda_{\text{exc}}$ : 285 nm,  $f_{\text{exc}}$ : 2.5 nm,  $f_{\text{em}}$ : 2.5 nm, temperature  $\approx 25$  °C) for 0, 90, 150, 210, 280 and 390 min.

Fig. 9. Mass fragmentation pattern of compound **2**.

the formula  $\text{C}_{21}\text{H}_{25}\text{O}_4$  ( $-0.2$  ppm). No study was made for the second ion. The ESI(+) mass spectrum of the dibenzodioxocin **2** showed two main ions at  $m/z$  979 and 479, corresponding to the formation of respectively, the cationized dimer  $(M + M + \text{Na})^+$  and the protonated one  $(M + \text{H})^+$  ( $M_W = 478$ ). The CID technique shows that the  $m/z$  479 ion gave the daughter ion  $m/z$  341. High resolution measurement (EI) indicates that there is a loss of a  $\text{C}_8\text{H}_9\text{O}_2$  radical between the molecular ion ( $M^+$ : 478) and the ion at  $m/z$  341. A similar observation was made in the mass spectrum of non-phenolic dibenzodioxocin **1**, already described [23]. A mechanism for the formation of the ion  $m/z$  341 is proposed in Fig. 9. The same ion was also observed in the spectrum of compound **6** (vide infra) and in many products described by Brunow's group [20]. This observation supports our conclusion on the structure of compound **6**.

A hypothetical scheme for the formation of photoproduct **4**, **6** and oligomers is proposed in Fig. 10. The first step of the photodegradation of dibenzodioxocin **2** is an ionic  $\alpha$ -O-4 cleavage, giving a quinone-methide. Similar formation of quinone methide (QM) was already observed by Leary [25] by laser flash photolysis on coniferyl alcohol. The QM might undergo ground state nucleophilic attack by ethanol. Quinone-methide might also induce  $\beta$ -O-4 bond cleavage,

as  $\alpha$ -carbonyl do in phenacyl-aryl ethers [7]. This cleavage gives phenoxy radical on the biphenyl part of the molecule in addition to an other radical, which might be written as a styrene-phenoxy radical. The two radicals might condense into unidentified oligomers or, for the biphenyl-phenoxy radical, to be converted into compound **4**, by hydrogen abstraction from an ethanol molecule or a phenolic group.

A possible pathway to give compound **6** is reported in Fig. 10. The biphenyl monophenol, obtained by addition of ethanol on the QM, might be oxidized into a phenoxy radical. The latter might react with an ethanol ketyl-type radical, probably formed by photooxidation of the solvent [33,34]. Oxidation of the benzylic hydrogen of the adduct might form the corresponding hydroperoxide, which is converted into the aromatic ketone **6**, after elimination of ethyl hydroperoxide.

The low reactive photoefficiency of phenolic dibenzodioxocin is probably due to the reversible formation of QM, which might undergo nucleophilic attack by the phenolic group of the biphenyl at the  $\alpha$ -carbon, giving back the dibenzodioxocin molecule **2**.

The fraction isolated with pure methanol (see Section 2) is composed of a mixture of not well-defined compounds, likely formed from biphenylbiphenol **4** [23] and/or a quinone methide radical (Fig. 10).

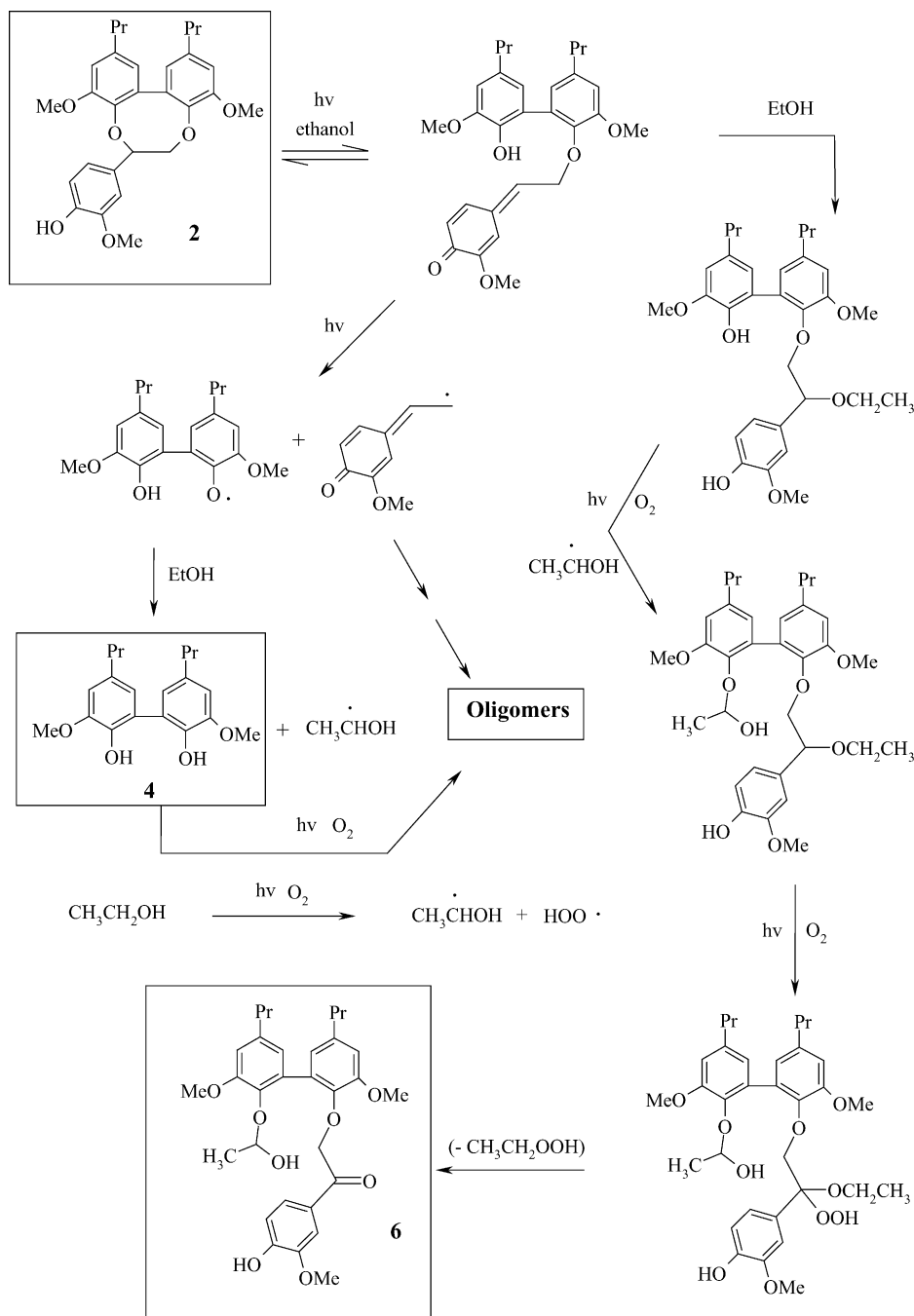


Fig. 10. Hypothetical formation pathways of compounds **4**, **6** and oligomers after photoirradiation of phenolic dibenzodioxocin molecule **2** in ethanol solution.

#### 4. Conclusion

We have shown very recently [23] that non-phenolic dibenzodioxocins (DBDO), which are considered as main branching element of the lignin polymer, are very efficiently photodegraded by UV-light ( $\phi_r > 0.3$ ) by successive cleavage of  $\alpha$ -O-4 and  $\beta$ -O-4 bonds. This process gives colored oligomers and likely a decrease of the branching structural network. The presence of a phenolic group on the C<sub>9</sub> part of

the DBDO framework leads to an important decrease of the photodegradation efficiency ( $\phi_r \approx 0.015$ ). Mass spectrometry analysis of the photoproducts suggests that reversible formation of intermediate quinone-methide might account for this decrease. Due to the low proportion of phenol in lignins (0.1/C<sub>9</sub> of lignin polymer [35]), dibenzodioxocin elements in lignocellulosics are probably etherified in large proportion and should be considered as important contributors to the photoreactivity of these materials. Studies on the partici-



pation of dibenzodioxocins to lignocellulosic photoreactivity are under way.

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