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Photochemical study of an *o*-ethyl dibenzodioxocin molecule as a model for the photodegradation of non-phenolic lignin units of lignocellulosics

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Abstract

The photochemical behavior of compound **1** was studied as representative of a non-phenolic dibenzodioxocin lignin model, because the presence of both photoreactive α-O-4 and β-O-4 linkages in these structures should bring a high photosensivity of the framework. Fluorescence emission of **1** is situated at shorter wavelength (340 nm) than the emission of the corresponding biphenylbiphenol **5** (380 nm). This observation, which has to be correlated with conjugation between the phenyl rings of the biphenyl chromophore, indicates that dibenzodioxocins are not contributing to the long wavelength emission in lignins (>480 nm). Irradiation of **1** in non-degassed benzene solutions, using Pyrex vessel, which eliminates wavelengths below 290 nm, gives colored solutions. The reaction is very efficient ($\Phi_R = 0.37$) and analysis of the photoproducts indicates that the first step of the reaction is a cleavage of the α-O-4 bond followed either by β-O-4 cleavage or formation of rearranged products. The color is due to condensation of biphenyl-oxidized products (quinone type). A mechanism is proposed based on separation and identification of photoproducts. The reactivity of **1** supports the fact that dibenzodioxocins have to be considered as important chromophores in photodegradation of lignocellulosic materials.

Keywords: Dibenzodioxocins; Lignin models; Fluorescence; Photoreactivity

1. Introduction

The high sensitivity of mechanical pulps and clear woods towards sunlight exposure is a well-described process [1–3]. It is generally accepted that the photoyellowing of lignocellulosics is mainly due to the photooxidation of lignin [2]. A lot of investigations have been carried out to elucidate the photoyellowing mechanism of wood and lignin containing papers [3]. It has been shown that phenoxy radicals are key intermediates in the photoyellowing process and they readily oxidize to form colored compounds in lignin [2]. Among them, *o*-benzoquinones were detected during the early stages of the photoyellowing [4]. Phenoxy radicals are formed through a variety of pathways: hydrogen abstraction of phenol hydrogen by excited α-carbonyl [5] or singlet oxygen [6], direct oxidation of phenols absorbing near-UV light [7], photocleavage of phenacylaryl ethers [8] and breakdown of the β-O-4 bond in arylglycerol-β-aryl ethers [9]. Alternatively, it has been proposed that the systems hydroquinone/*p*-benzoquinone are important structures in the yellowing process of lignocellulosics [10–16]. Hydroquinones belong to phenol structures that absorb light in low wavelengths between 300 and 400 nm and they are reactive in lignocellulosics. By contrast, some studies on other conjugated phenol chromophores, such as coniferyl alcohol [17] and stilbene structural elements [18,19], indicate that these structures are not at the origin of the photoyellowing. They mainly have a photophysical influence on lignins by increasing their fluorescence intensity. Among non-phenolic lignin structures, efficient photochemical degradation ($\Phi_R \approx 0.2$–0.3) through α-C–O bond cleavage was evidenced for benzylaryl ether units [20].

The proportion of biphenyl units is abundant in softwood lignins (15–25%) [21,22]. Most of them are etheri-

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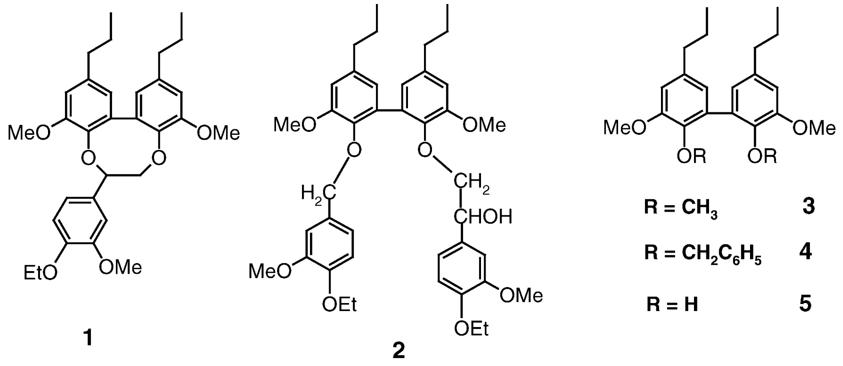


Scheme 1. Formulae of compounds involved in the study.

fied [23,24]. Brunow's group showed that a large part of these structures are etherified by α and β carbons of another phenylpropane unit giving an eight-membered ring, dibenzodioxocin [25–27]. Dibenzodioxocins are considered as main branching points in lignins [25]. During secondary wall thickening, the dibenzodioxocin structure is more abundant in the secondary cell wall layers than in the middle lamella [28]. In mature cells these structures are observed in the S3 layer in Norway spruce and in Silver birch [29]. Dibenzodioxocins were considered as structural elements involved in chemical pulping and bleaching [30–32]. Because biphenyl units present absorption above 300 nm, where sunlight is active, they might be important chromophores in photochemical degradation of lignocellulosics. Moreover contribution of biphenyl structures to the fluorescence properties of wood and high-yield pulps is still controversial [33]. Photophysical and photochemical properties of dibenzodioxocins remain unknown; however the presence of both photoreactive α-O-4 and β-O-4 linkages should bring a high photosensivity to the framework. In this article, the photochemical behavior of compound **1** (Scheme 1), a non-phenolic dibenzodioxocin lignin model, is reported. Its photodegradation in dilute solution, monitored by UV-Vis absorption spectroscopy, was compared with those of other biphenyl derivatives **2**–**4** in order to approach the role of dibenzodioxocin ring in the photoreactivity. Moreover, the fluorescence emission spectra of these compounds were measured to evaluate whether the dibenzodioxocin structure might be a good candidate to explain the long wavelength emission in lignocellulosics. Some products obtained by irradiation of compound **1**, in more concentrated solutions, have been unambiguously identified.

2. Experimental

2.1. General

The starting materials and solvents of appropriate grade (for synthesis or for spectroscopy) were obtained from Aldrich and used without further purification. Studies by ^{1}H NMR were made using Bruker AC250 Fourier transform spectrometer (solvent: CDCl$_3$). *J* values are given in Hz. UV-Vis spectra were recorded on a Lambda 18 Perkin-Elmer spectrometer for polychromatic irradiations and with a Perkin-Elmer HP8452A diode array spectrophotometer for monochromatic irradiations (reactivity quantum yield). FT-IR spectra were made with a Perkin-Elmer Paragon 1000 PC spectrometer. Low resolution mass spectra were recorded using a Finnigan Trace mass spectrometer and high resolution mass spectra were obtained using a VG Micromass AutoSpec Q (electronic ionization mode 70 eV).

Products were purified by column chromatography using Merck silica gel 60. TLC analyses were carried out on Fluka silica gel F$_{254}$ plates (thickness 0.20 mm) and on Macherey–Nagel Alugram RP-18W/UV254 plates (thickness 0.15 mm).

The photoproducts obtained by irradiation of compound **1** were analyzed with the Finnigan Trace mass spectrometer interfaced with a Finnigan Trace GC Ultra gas apparatus (line transfer temperature: 250 °C) equipped with a PTV injector (splitless mode) using Helium as a carrier gas. A fused silica capillary RTX-5MS column, 15 m × 0.25 mm i.d., film thickness 0.25 μm was selected. The oven temperature was programmed typically from 40 °C (initial hold time of 1 min) to 320 °C at a rate of 15 °C min^{-1}; this final temperature was maintained for 15 min. The electron energy was fixed at 70 eV.

2.2. Photochemical techniques

2.2.1. Polychromatic irradiations

Photodegradation of compounds **1**–**4**, in methanol or benzene solution (concentration $\approx$3–5$\times$10^{-4} mol L^{-1}), in a 1 mm quartz cell, were monitored by UV absorption spectroscopy at different reaction times. The irradiation device included two parallel medium-pressure mercury lamps (400 W), a fan directed towards the sample to maintain temperature at $\approx$30 °C. To eliminate wavelengths below 300 nm, a Pyrex container surrounded the sample cell. Oxygen was excluded of the solution by bubbling nitrogen gas for 15 min. In order to isolate some photoproducts, more concentrated solutions of compound **1** in benzene (concentration $\approx 2\times10^{-3}$ mol L^{-1}) were irradiated with the same setup. A typical reaction is given in the following part. Dibenzodioxocin **1** (125 mg, 0.25 mmol) was diluted in benzene (120 mL) and irradiated during 5 h using the experimental device described above. After elimination of the solvent under vacuum (30 °C), the residue (133 mg) was chromatographed on silica gel giving six main fractions. The products present in the first fraction (light petroleum ether/methylene chloride 9/1 (v/v), 8 mg) were identified by GC-MS as phenol and biphenyl (mass spectra and authentic samples). In the second fraction (methylene chloride, 17 mg), two main products: 4-ethoxy-3-methoxy styrene **11** and 4-ethoxy-3-methoxy benzaldehyde **12**, present in equal proportions, were identified by their typical mass spectra [34,35] and by comparison with authentic synthesized samples [35]. Unreacted dibenzodioxocin **1** was the main product of the third fraction (methylene chloride, 35 mg). The fourth fraction (methylene chloride–ethyl ether 9/1 (v/v), 10 mg) was composed by several compounds, which after many attempts have not been identified. The fifth fraction (methylene chloride–methanol 9/1 (v/v), 16 mg) was attributed to 4-ethoxy-3-methoxybenzoic acid by GC-MS after silylation of the sample by reference to the corresponding synthesized compound. Analysis of the sixth fraction (methylene chloride–methanol 8/2 (v/v), 47 mg) by TLC with different eluent mixtures on direct and C_{18} silica plates did not allow separation of determined compounds. Mass spectrometry analysis did not give conclusive structural attribution.

2.2.2. *Disappearance quantum yield determination of compound* **1**

Irradiation was performed using a 2 kW xenon arc coupled to an irradiation monochromator (Jobin–Yvon) providing about 3×10^{15} photons cm^{-2} s^{-1} on a 4 nm spectral bandwidth at 295 nm. The disappearance rates of compound **1** in benzene d_6 (3 ml, concentration $\approx 2\times10^{-3}$ mol L^{-1}) was determined by ^{1}H NMR using Me-O-*t*-Bu, as internal standard. The conversion rate was limited to 10%, in order to estimate the disappearance quantum yields. Under these conditions, the absorption was total and mainly due to starting material. The relative conversion rate repeatability was ±7%.

The flux of photons irradiating the sample (same position of the cell) was obtained by actinometry using the photocoloration of a toluene solution of Aberchrome 540 [36] (3 ml, 5×10^{-3} mol L^{-1}) which absorbs totally the photons at 295 nm. The coloration of Aberchrome 540 was measured at 494 nm ($\Phi_R = 0.2$ and $\varepsilon_{494} = 8200$ L mol^{-1} cm^{-1}). The accuracy of the quantum yield was estimated ±15%.

2.2.3. *Fluorescence measurements*

Fluorescence spectra were recorded with a Hitachi F4500 apparatus at room temperature ($\approx$20 °C). The slits on the excitation and emission beams were respectively fixed at 2.5 and 5 nm, the emission spectra were corrected for instrumental response. The fluorescence quantum yields were determined using biphenylbiphenol **5**, as standard [38]. The concentrations were adjusted near 10^{-5} mol L^{-1}. The solutions were degassed by nitrogen bubbling before measurements.

2.3. *Syntheses*

2.3.1. *General*

A general scheme describing the syntheses performed for this study is given in Fig. 1. The syntheses of biphenyls **3** and **5** were already described [7,17]. BrAvBn and BrAvEt compounds were prepared in 77 and 60% yields, respectively, from acetovanillone by conventional methods [26,27,39]. 4-Ethoxy-3-methoxybenzyl bromide was synthesized in 48% yield according to standard methods [20] from vanillin after ethylation of the phenol group, $NaBH_4$ reduction of the aldehyde group followed by bromination of the benzyl alcohol by PBr_3.

4-Ethoxy-3-methoxystyrene **11** was prepared by ethylating commercial 4-vinylguaiacol. It was characterized by ^{1}H NMR spectroscopy [($CDCl_3$) δ ppm: 1.43 (t, 3H, CH_3), 3.85 (s, 3H, OCH_3), 4.06 (q, 2H, OCH_2), 5.09–5.2 (m, 1H, =CH), 5.50–5.70 (m, 1H, =CH), 5.90–6.75 (m, 1H, HC=), 6.75–7.0 (m, 3H, ArH)] and mass spectrometry [35]. 4-Ethoxy-3-methoxybenzoic acid **13** was prepared by ethylation of vanillic acid according to Mamer et al. [37] and silylated by BSTFA/TMCS in acetonitrile.

2.3.2. *2,2′-Bis-benzyloxy-3,3′-dimethoxy-5,5′-dipropyl-biphenyl* **4**

A solution of compound **5** (1.43 g, 4.3 mmol) in THF (100 mL) under nitrogen atmosphere was treated with potassium hydroxide (900 mg, 16 mmol) in water (3 mL) and benzyl bromide (2.74 g, 16 mmol). The mixture was stirred at 70 °C for 20 h. After elimination of the solvent in vacuum, the residue was extracted with dichloromethane (70 mL). After usual workup of the organic phase, the product was purified by column chromatography on silica gel (eluent, dichloromethane–diethyl ether 95/5 (v/v)) affording **4** as an oily compound (1.47 g, yield 67%). ^{1}H NMR ($CDCl_3$) δ ppm: 0.97 (m, CH_3, 6H), 1.55–1.75 (m, CH_2, 4H), 2.59 (t, CH_2, 4H), 3.91 (s, OCH_3, 6H), 4.78 (s, OCH_2, 4H), 6.6–6.9 (m, ArH, 4H). 7.05–7.45 (m, ArH, 10H). MS *m/z* 510 (M^+, 4%,), 328 (10%), 327 (12%), 299 (18%), 297 (13%), 129 (20%), 91 (100%).

2.3.3. *6-(4-Ethoxy-3-methoxyphenyl)-4,9-dimethoxy-2,11-di-n-propyl-6,7-dihydro-5,8-dioxa-dibenzo[a,c]cyclooctene,* **1** *(dibenzodioxocin)*

The experimental procedure to prepare the phenolic dibenzodioxocin **8** is similar to the description given by Brunow's group [26,27]. The yields of the reactions in our hands are given in Fig. 1. Compound **8** was characterized by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$) δ ppm: 0.95–1.1 (m, CH_3, 6H), 1.7 (m, CH_2, 4H), 2.6 (m, CH_2,

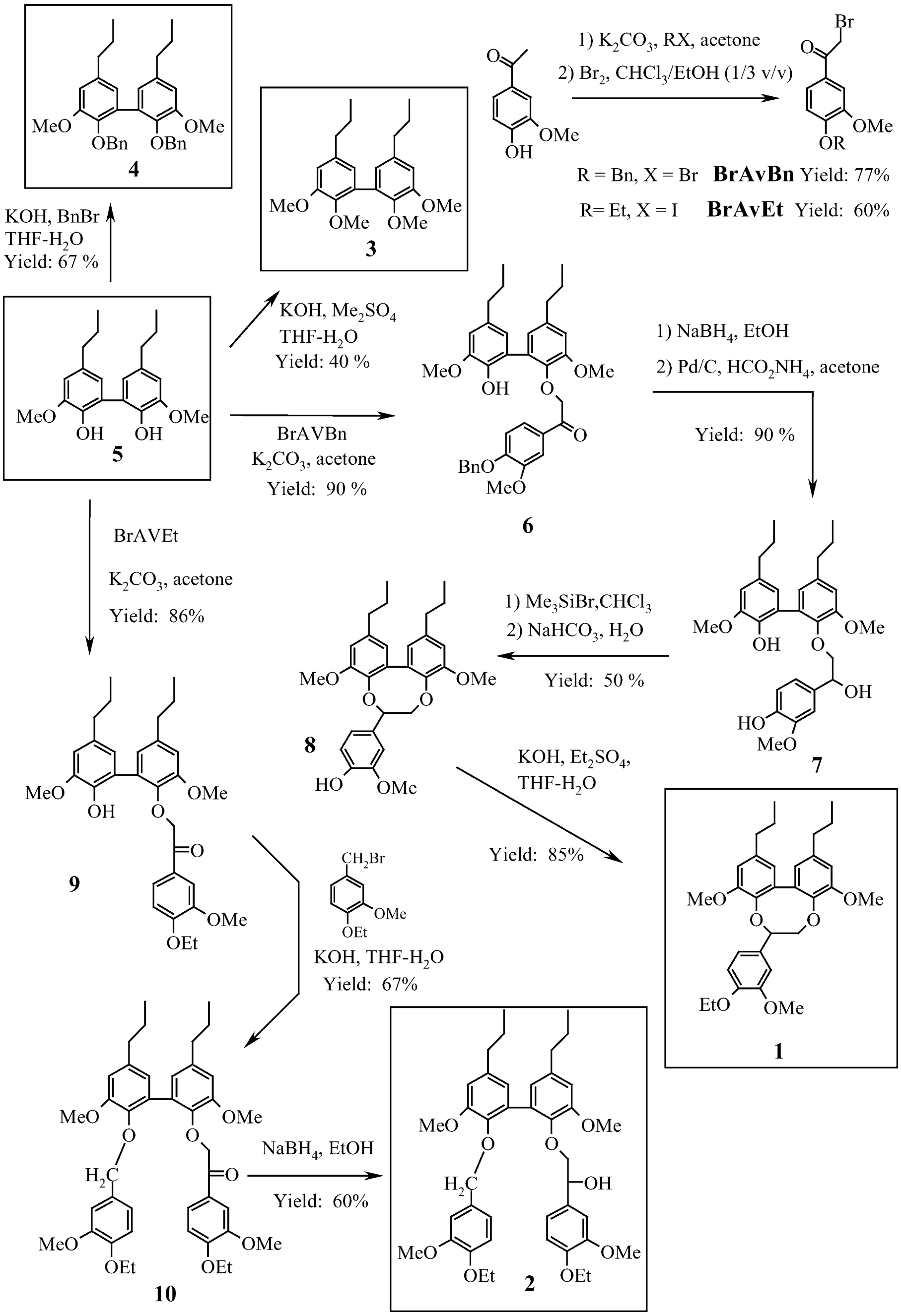


Fig. 1. Synthesis of the studied biphenyl compounds.

4H), 3.84–3.98 (m, H_β, 1H), 3.79 (s, OCH_3, 3H), 3.90 (s, OCH_3, 3H), 3.93 (s, OCH_3, 3H), 4.5 (dd, $J_1 = 3.2$ and $J_2 = 11.7$, H_β, 1H), 4.95 (dd, $J_1 = 3.2$ and $J_2 = 11.7$, H_α, 1H), 5.95 (s, OH, 1H), 6.7–7.3 (m, ArH, 7H). These chemical shifts are very similar to those given for the acetylated derivative [27].

Compound **1** was obtained by ethylating the phenol group by diethyl sulfate. A solution of compound **8** (460 mg, 0.96 mmol) in THF (30 mL) under nitrogen atmosphere was treated with potassium hydroxide (54 mg, 0.96 mmol) in water (5 mL) and with an excess of diethyl sulfate (2 mmol). The mixture was stirred at 70 °C for 12 h. After elimination of the solvent in vacuum, the residue was extracted with dichloromethane (70 mL). After usual workup of the organic phase, the product was purified by column chromatography on silica gel (eluent, dichloromethane–diethyl ether 95/5 (v/v)) affording the dibenzodioxocin **1** as a white powder (320 mg, yield 85%), mp 144 °C. ^1H NMR ($CDCl_3$) δ ppm: 1.0 (m, CH_3, 6H), 1.5 (t, CH_3, 3H), 1.7 (m CH_2, 4H), 2.65 (m, CH_2, 4H), 3.6–4.0 (m, H_β, 1H), 3.77

(s, OCH_3, 3H), 3.89 (s, OCH_3, 3H), 3.90 (s, OCH_3, 3H), 4.1 (q, OCH_2, 4H), 4.5 (dd, $J_1 = 3.2$ and $J_2 = 11.7$, H_β, 1H), 4.95 (dd, $J_1 = 3.2$ and $J_2 = 11.7$, H_α, 1H), 6.6–7.2 (m, ArH, 7H). IR (KBr) ν: 2965, 2930, 2870, 2855, 1585, 1510, 1465, 1415, 1385, 1266, 1261, 1230, 1140, 1050, 1030, 920, 845, 820, 805, 725 cm^{-1}. MS *m/z* 506 (M^+, 100%, 341 (59%), 299 (54%), 178 (18%), 165 (35%), 150 (32%); HRMS: measured mass *m/z* 506.266766, $C_{31}H_{38}O_6$ requires 506.266840.

2.3.4. 2-[4-Ethoxy-3-methoxy-benzyloxy]-2′-[1-hydroxy-2-(4-hydroxy-3-methoxy)-ethoxy]-3,3′-dimethoxy-5,5′-di-n-propyl-biphenyl, 2

Compound **9**: The biphenyl compound **5** (2.18 g, 6.6 mmol) was dissolved in acetone (80 mL) to which dry potassium carbonate (1.82 g, 13.2 mmol) and the bromo ketone BrAvEt (1.8 g, 6.6 mmol) were added. The mixture was vigorously stirred for 15 h at room temperature under nitrogen atmosphere. After separation of the solid compound, elimination of the solvent in vacuum, the residue was chromatographed on silica gel (eluent: dichloromethane–diethyl ether 95/5 (v/v)) giving **9** as an oily compound (2.95 g, yield 86%). ^1H NMR ($CDCl_3$) δ ppm: 1.0 (m, CH_3, 6H), 1.5 (t, CH_3, 3H), 1.7 (m CH_2, 4H), 2.65 (m, CH_2, 4H), 3.77 (s, OCH_3, 3H), 3.89 (s, OCH_3, 3H), 3.90 (s, OCH_3, 3H), 4.1 (q, OCH_2, 4H), 5.1 (s, $OCH_2C{=}O$, 2H), 6.4–6.8 (m, ArH, 7H).

Compound **10**: A solution of compound **9** (700 mg, 1.34 mmol) in THF (25 mL) under nitrogen atmosphere was treated with potassium hydroxide (300 mg, 5.36 mmol) in water (2 mL) and then 4-ethoxy-3-methoxybenzyl bromide (490 mg, 2 mmol). The mixture was stirred at 70 °C for 20 h. After elimination of the solvent in vacuum, the residue was extracted with dichloromethane (70 mL). After usual workup of the organic phase, the product was purified by column chromatography on silica gel (eluent, dichloromethane–diethyl ether 95/5 (v/v)) affording **10** as an oily compound (620 mg, yield 67%). ^1H NMR ($CDCl_3$) δ ppm: 0.9 (m, CH_3, 6H), 1.5 (t, CH_3, 6H), 1.7 (m CH_2, 4H), 2.5 (q, CH_2, 4H), 3.7 (s, OCH_3, 3H), 3.77 (s, OCH_3, 3H), 3.89 (s, OCH_3, 3H), 3.90 (s, OCH_3, 3H), 4.0 (q, OCH_2, 4H), 4.6 (s, OCH_2Ph, 2H), 4.9 (s, $OCH_2C{=}O$, 2H), 6.4–7.2 (m, ArH, 10H).

Compound **2**: To compound **10** (500 mg, 73 mmol), dissolved in ethanol (25 mL) was added sodium borohydride (120 mg, 3.15 mmol). The mixture was stirred for 4 h at room temperature, and neutralized with dilute hydrochloric acid. Usual workup and chromatography on silica gel (eluent, dichloromethane–diethyl ether 95/5 (v/v)) afforded compound **2** as oil (300 mg, yield 60%). ^1H NMR ($CDCl_3$) δ ppm: 0.9 (m, CH_3, 6H), 1.5 (t, CH_3, 6H), 1.7 (m CH_2, 4H), 2.5 (q, CH_2, 4H), 3.4 (m, OCH_2CHOH, 2H), 3.7 (s, OCH_3, 3H), 3.71 (s, OCH_3, 3H), 3.89 (s, OCH_3, 3H), 3.90 (s, OCH_3, 3H), 3.95 (q, OCH_2, 4H), 4.6 (m, CHOH, 1H), 4.7 (s, OCH_2, 2H), 6.4–6.9 (m, ArH, 10H). IR (film) ν: 3525, 2960, 2930, 2870, 1580, 1515, 1460, 1455, 1420, 1265, 1230, 1140, 1090, 1040, 1005, 860, 845, 800 cm^{-1}. MS *m/z* 688 (M^+, 0.01), 671 (1%), 507 (13%), 165 (100%), 137 (80%).

3. Results and discussion

3.1. Synthesis of model compounds 1–5

The preparation of compound **1**, based on Brunow's group work [27], is shown in Scheme 1. The synthesis involves oxidative dimerization of isoeugenol, a cheap commercial compound, followed by catalytic hydrogenation of the double bonds. Condensation of the bromo ketone BrAvBn on the diphenol **5**, followed by reduction of the carbonyl group and debenzylation, leads to compound **7**. Phenolic dibenzodioxocin **8** is obtained by nucleophilic attack of the phenol group to the quinone-methide, formed by addition of trimethylbromosilane on compound **7** and treatment with sodium hydrogenocarbonate. The phenol group of compound **8** was ethylated to give the model compound **1**, in order to discriminate meta and para positions of the phenylethane element. The global yield from isoeugenol is 15%.

To obtain complementary mechanistic information on the photophysics and photochemistry of non-phenolic dibenzodioxocins, the model compounds **2**–**5** were synthesized.

Compound **5** is a reference compound for fluorescence quantum yield determination and for its photoreactivity as phenol absorbing light above 300 nm [7] and compound **3** represents a non-phenolic biphenyl lignin model, with very low reactivity [7]. In compound **4**, the presence of two benzyloxy groups mimics two α-O-4 structural elements able to generate, by irradiation, phenoxy radicals, which are later converted into quinonoid colored structures [20]. Compounds **3** and **4** were prepared by the reaction of dimethyl sulfate or benzyl bromide on the diphenol **5**, respectively.

Compound **2**, a non-cyclic biphenyl model compound, including photoreactive α-O-4 and β-O-4 elements, is synthesized using a similar procedure adopted for compound **1** with BrAvEt instead of BrAvBn. Condensation of 4-ethoxy-3-methoxybenzyl bromide and reduction of the α-carbonyl group gave compound **2**. The ethoxy group in 4-position of the α-O-4 and β-O-4 elements in compound **2** was chosen to differentiate it from methoxy group and also for its photochemical inertia compared to benzyloxy group. The global yield starting from **5** is 34%.

3.2. Absorption and fluorescence spectra of compounds 1–5

The electronic absorption spectra of the biphenyl model compounds **1**–**5** in methanol solutions are shown in Fig. 2.

The absorption spectrum of dibenzodioxocin **1** extends to 310 nm, with two intense bands at 203 and 219 nm, a small shoulder near 253 nm, and a low intensity band at 280 nm. The latter can be attributed to a charge-transfer transition between the phenyl groups of the biphenyl chromophore;

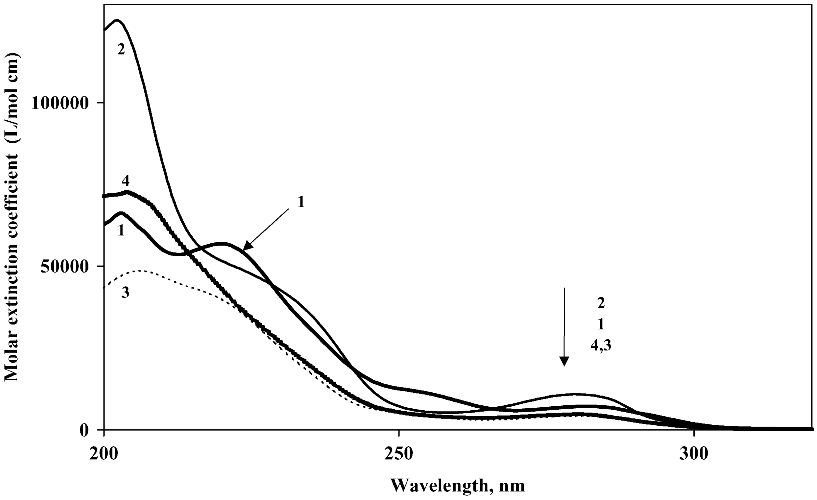


Fig. 2. Electronic absorption spectra of biphenyl model compounds **1**–**4**.

this band is present in all the studied compounds. The 253 nm band appears to be specific of the dibenzodioxocin structure.

The fluorescence of lignocellulosic materials is quite controversial from the point of view of the fluorophores responsible for the fluorescence emission. Olmstead and Gray [40] proposed that fluorescence of lignocellulosics is mainly due to cellulose, the lignin polymer acting as inner filter. By contrast Castellan's group proposed that structures such as biphenyl, coniferyl alcohol, and phenylcoumarone and other stilbene elements, present in lignin molecule, are responsible for emission at about 400 nm [41–43], in accordance with Lundquist and coworkers' studies [33]. The origin of lignin emission at 480 nm remains unknown. The presence of dibenzodioxocins, as new structures in lignocellulosic materials incites us to evaluate their potential contribution to the long wavelength emission of lignin.

Table 1
Fluorescence quantum yields of biphenyl compounds **1**–**5** in degassed methanol (concentration $\approx 10^{-5}$ mol L^{-1})

Biphenyl compounds	Φ_F (degassed solution)
1	0.15
2	0.08
3	0.04
4	$<10^{-2}$
5	0.33

The fluorescence emission spectra for compounds **1**–**5** were measured in dilute methanol solutions (Fig. 3) and their fluorescence quantum yields (Table 1) were determined by reference to compound **5** [38].

The dibenzodioxocin **1** shows a maximum of fluorescence emission at 345 nm which is at shorter wavelength than those

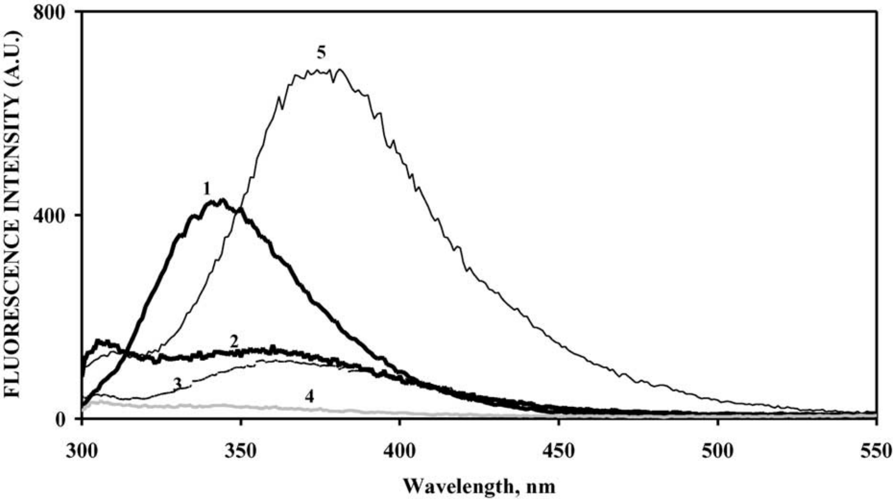


Fig. 3. Fluorescence emission spectra of biphenyl compounds **1**–**5** in degassed methanol (concentration $\approx 10^{-5}$ mol L^{-1}, λ_{exc}: 280 nm, f_{exc}: 2.5 nm, f_{em}: 5 nm).

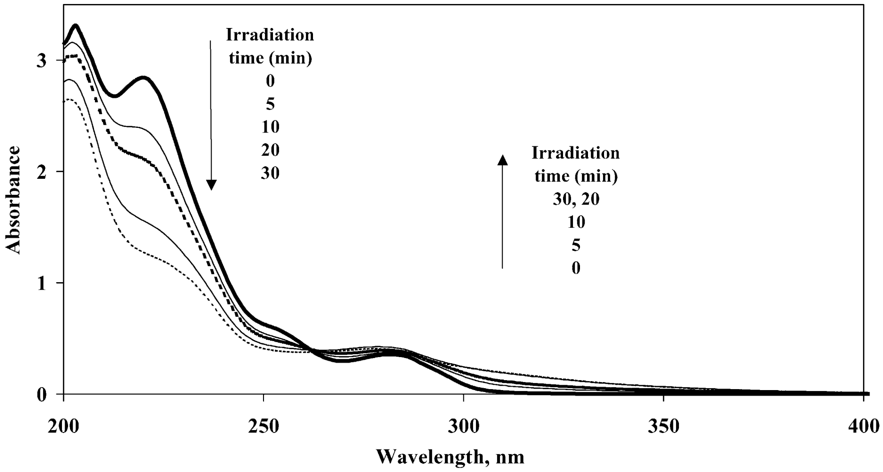


Fig. 4. Absorption spectra of compound **1** after polychromatic irradiation (see Section 2) in non-degassed methanol solution (concentration ≈5×10^{-4} mol L^{-1}, path length: 1 mm, temperature ≈30 °C) for 0, 5, 10, 20, and 30 min.

of biphenyl **2** (360 nm) and diphenol **5** (380 nm). This hypsochromic effect is likely related to the torsion angle of the phenyl groups in the biphenyl moiety. This angle should be minimum in diphenol **5**, due to some intramolecular hydrogen bonding between the phenolic groups; the maximum emission of compound **2**, should correspond to the usual twist angle found in biphenyls [44]. The eight-member ring of dibenzodioxocin induces some constraints that increase the non-planarity of both phenyl groups [26].

The highest quantum yield is found for diphenol **5**; etherification of the phenolic groups (compounds **1**–**4**) leads to important decrease of the emission intensity. The relative decrease is difficult to explain in terms of electronic states, the absorption spectra of the different compounds being similar. The differences are likely related to different vibration modes that contribute to the internal conversion process.

According to these fluorescence observations, it can be concluded that dibenzodioxocin structural elements in lignin are not at the origin of the long wavelength emission (480 nm).

3.3. Photochemistry

The photoability to give yellow compounds has been previously described in dilute alcohol solution for various lignin models, including the biphenyls **3** and **5**, the phenolic one being the most sensitive [38]. We have recorded the absorption spectra of dilute methanol and benzene solutions (degassed or non-degassed) of compounds **1**–**4** irradiated with polychromatic light for different periods of time. Degassing does not affect in a large extend the curve evolution, and the behavior of compounds in benzene and methanol is very similar. The absorption curves for non-degassed methanol solutions between 200 and 400 nm are presented in Figs. 4–7. The curves obtained for benzene solutions are less informative because wavelengths

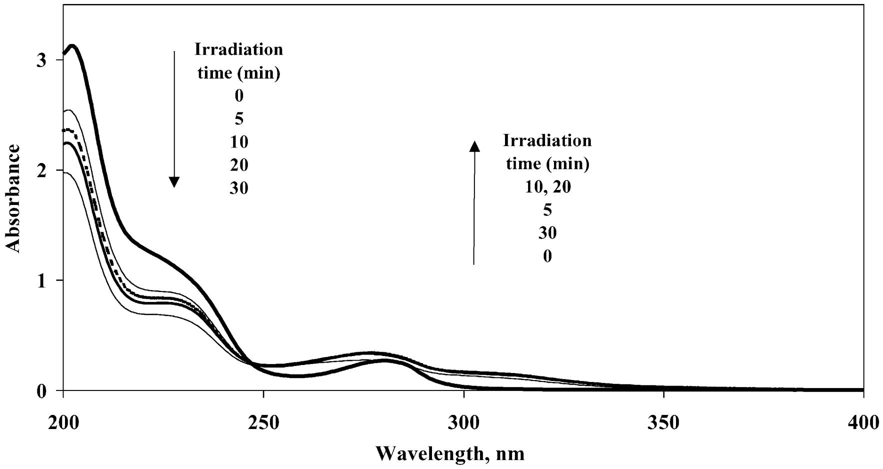


Fig. 5. Absorption spectra of compound **2** after polychromatic irradiation (see Section 2) in non-degassed methanol solution (concentration ≈2.5×10^{-4} mol L^{-1}, path length: 1 mm, temperature ≈30 °C) for 0, 5, 10, 20, and 30 min.

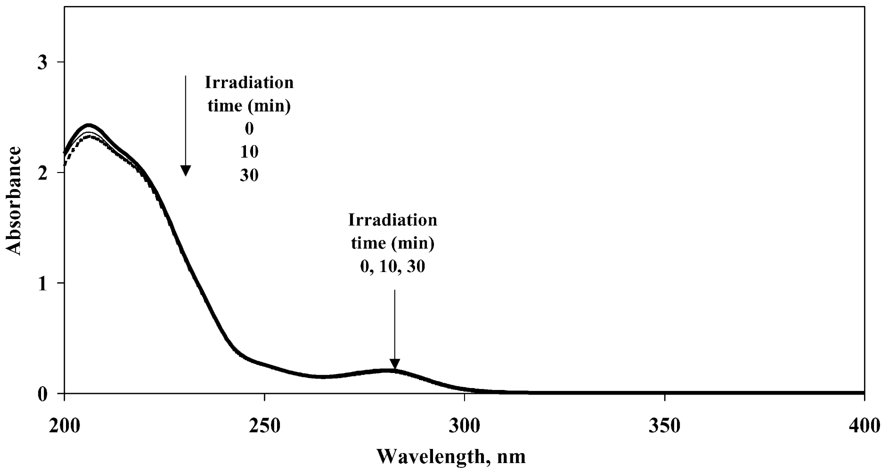


Fig. 6. Absorption spectra of compound **3** after polychromatic irradiation (see Section 2) in non-degassed methanol solution (concentration $\approx 5\times10^{-4}$ mol L^{-1}, path length: 1 mm, temperature ≈30 °C) for 0, 10, and 30 min.

less than 280 nm are not significant, due to solvent absorption.

Comparison of Figs. 4–7 indicates that the photoreactivity is in the order dibenzodioxocin **1** > biphenyl including α-O-4 and β-O-4 substituents **2** > dibenzyloxy biphenyl **4** > tetramethoxybiphenyl **3**, the latter being almost non-reactive. Disappearance quantum yield of dibenzodioxocin **1** in d_6 benzene was measured to be 0.37, indicating a very high photochemical efficiency. This value is close to those found for α-O-4 cleavage for non-phenolic benzylaryl ether units (0.2–0.3) [20]. The β-O-4 bond cleavage in arylglycerol-β-aryl ethers was found quite inefficient in non-sensitized irradiation [45]. Consequently, the high reactive quantum yield of compound **1** is in favor of an α-O-4 cleavage in the first step of the photochemical degradation. The photoreactivity of compounds **2** and **4** is likely due to the same chromophore.

To assess the mechanism of photodegradation of non-phenolic dibenzodioxocins, compound **1** was irradiated in more concentrated benzene solution ($\approx 2\times10^{-3}$ mol L^{-1}). The reaction mixture was separated by column chromatography on silica gel in six fractions (see Section 2). The less polar fraction (≈6% by weight) includes photoproducts of the solvent, phenol and biphenyl, easily identified by GC-MS. The second fraction (≈13% by weight) is constituted by 4-ethoxy-3-methoxystyrene, **11** and 4-ethoxy-3-methoxy benzaldehyde, **12** (1/1) identified by GC-MS with authentic samples. The third fraction (≈26% by weight) corresponds to unreacted dibenzodioxocin **1**. The fourth fraction (≈7% by weight) is composed of numerous defined non-identified compounds. The fifth fraction (≈12% by weight) was isolated practically pure and was attributed to 4-ethoxy-3-methoxybenzoic acid, **13**, by comparison (GC-MS) with an authentic silylated sample. The last isolated fraction (≈36% by weight) is constituted of a mixture of not well-defined oligomers, likely formed from the biphenyl part of the compound **1**. It is remarkable that compound **5** was not found in the photoirradiation mixture.

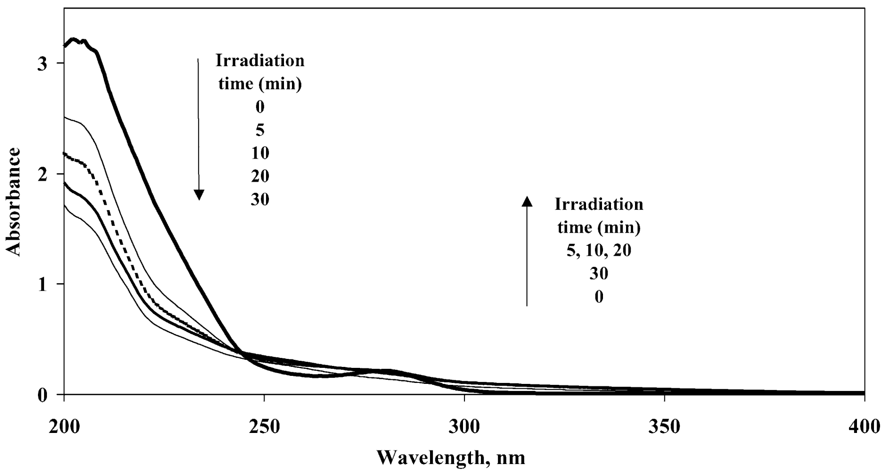
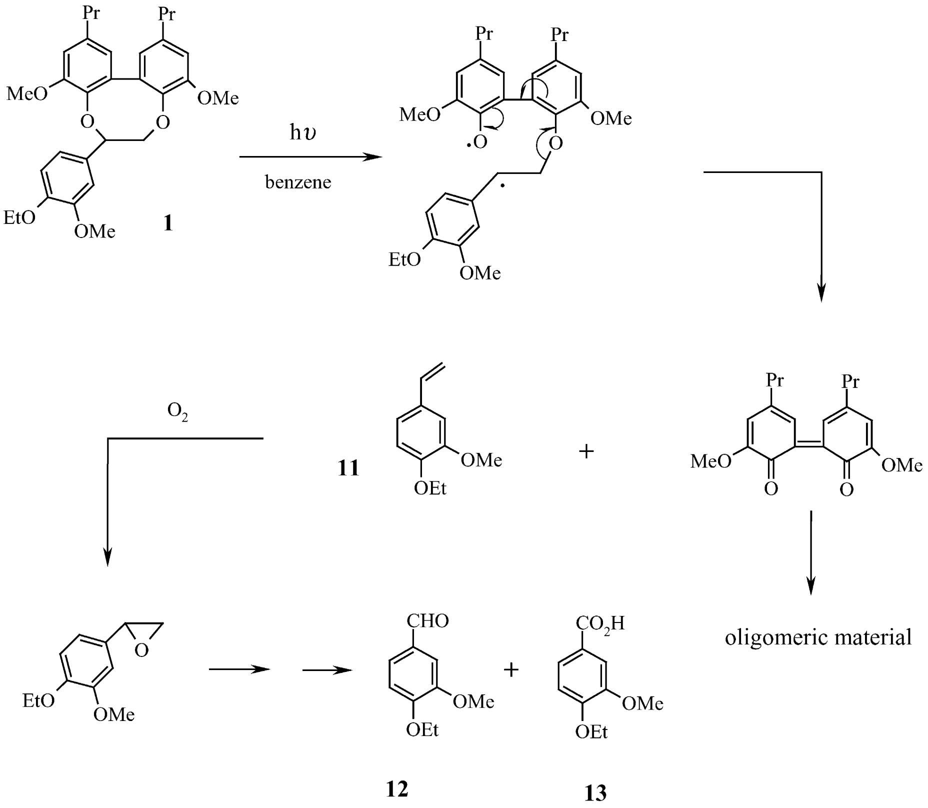


Fig. 7. Absorption spectra of compound **4** after polychromatic irradiation (see Section 2) in non-degassed methanol solution (concentration $\approx 5\times10^{-4}$ mol L^{-1}, path length: 1 mm, temperature ≈30 °C) for 0, 5, 10, 20, and 30 min.



Scheme 2. Photodegradation mechanism of non-phenolic dibenzodioxocin **1**.

The formation of oligomeric materials has been observed many times after irradiation of lignin model compounds [7,20,39].

The first step of the photodegradation of dibenzodioxocin **1** (Scheme 2) corresponds to the α-O-4 cleavage of the molecule followed by the β-O-4 bond scission induced by the benzylic radical as already shown by Scaiano et al. [9]. It is likely that the *ortho*-diketone formed in the process is converted into colored oligomeric material. Irradiation of the biphenylbiphenol **5** in similar experimental conditions also leads to some non-well defined oligomers. It has not been possible to identify the corresponding styrene oxide by GC-MS. It seems that it is converted into the aldehyde **12** and the carboxylic acid **13**. Diphenyl and phenol obtained in the first fraction are characteristic of benzene photoproducts when irradiated in aerated medium.

4. Conclusion

The recent discovery by Brunow's group of the existence of dibenzodioxocins in lignins as main branching element of the lignin polymer appeared a very important fact from a photochemical point of view because they contain both biphenyl groups, which absorb light above 300 nm where the sunlight emits, and α-O-4 and β-O-4 photoreactive structural elements. Although, phenolic groups in lignins remain an important cause of the polymer photodegradation, this study has shown that non-phenolic dibenzodioxocins are efficiently photocleaved ($\Phi_R > 0.3$), probably leading to a depolymerization of the branching structural network by UV light. In contrast to this photochemical importance, their fluorescence emission does not contribute more than other biphenyls to lignin fluorescence, especially to the unknown origin emission, in lignocellulosics, situated at long wavelengths. These conclusions concern non-phenolic dibenzodioxocins; however the presence of phenolic groups in these structural elements might affect their photophysical and photochemical properties. A similar study on a phenolic dibenzodioxocin model will be presented in a near future (Scheme 2).

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