Photoyellowing of peroxide-bleached lignin-rich pulps: a photochemical study on stilbene– hydroquinone chromophores issued from β -5 units of lignin during refining and (or) bleaching

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Abstract: The contribution of stilbene–parahydroquinone structures, formed from β -5 units during refining and bleaching, in photoreversion of peroxide-bleached high-yield pulps, was studied using 4'-benzyloxy-2,5-dihydroxy-3,3'-dimethoxystilbene (I), as a model compound. The various photoproducts formed during irradiation of I in solution or adsorbed on cellulose paper were identified. Isomerization of the stilbene double bond and oxidation of the hydroquinone into quinone were observed in solution, whereas in the solid state only the formation of the quinone was found to operate. Our attempts to detect and quantify stilbene–hydroquinones forming from β -5 units created on peroxide bleached mechanical pulp were not met with success.

Key words: lignin, stilbene, hydroquinone, lignin model compound, pulp, photoyellowing.

Résumé : La contribution des structures stilbène–parahydroquinone, formées à partir des unités β -5 durant le raffinage et le blanchiment de la pâte, au photojaunissement des pâtes mécaniques blanchies au peroxyde d'hydrogène a été étudiée à l'aide du 4'-benzyloxy-2,5-dihydroxy-3,3'-diméthoxystilbène (I). Les photoproduits formés sous irradiation de I en solution ou adsorbé sur papier de cellulose ont été identifiés. L'isomérisation de la double liaison stilbène ainsi que l'oxydation de l'hydroquinone en quinone ont été observées en solution, tandis qu'en phase solide, seule la formation de la quinone est notée. La détection et le dosage des unités stilbène-hydroquinone dans la pâte mécanique blanchie ne se sont pas révélés concluants.

Mots clés : lignine, stilbène, hydroquinone, composé modèle de la lignine, pâte, photojaunissement.

Introduction

High-yield pulps are obtained by mechanical refining of wood. This treatment causes some chemical modifications in the pulp and new chemical structures are formed. For example, phenylcoumaran (1, 2) and β -1 units (3) are turned into stilbenes by mechanochemistry, β -O-4 entities are converted into parahydroxybenzaldehyde (4), and coniferyl alcohols create α , β -unsaturated groups (5). Also acidic treatment generates stilbenes and phenylcoumarones (6) very sensitive to UV light (7, 8).

When lignin-rich pulps are bleached, new chromophores very sensitive to UV light are created. For example by the action of alkaline H_2O_2 bleaching solution, β -1 diol units are turned into stilbenes (9), α -carbonyl phenols were converted into hydroquinones (Dakin reaction) (10). In the same way, coniferaldehydes are transformed into methoxyhydroquinones

(11). All these chromophores, hydroquinones in particular, were considered to have a key role in the photoyellowing of bleached mechanical pulps because hydroquinones, non-colored compounds, are easily oxidized into quinones (12), (very colored species). Lee and Sumimoto (13) suggested that parahydrobenzoquinone derivatives including a stilbene or biphenyl or diphenyl ether conjugated structures were the major chromophores responsible of the color reversion of pulps.

In a recent study (14), we performed a semi-quantitative evaluation, in peroxide-bleached high-yield pulps, of *p*-stilbene phenols formed from β -1 units and demonstrated that they are not the main contributors of the rapid photoyellowing of these pulps. The present article describes a similar approach on the photochemical behavior of chromophores including both parahydroquinone and stilbene entities. In that respect, the photochemical behavior of model I (Fig. 1) before and after catalytic hydrogenation and (or) acetylation was established and also a tentative evaluation of the content of this type of structure in peroxide-bleached softwood mechanical pulps was carried out.

Experimental

1. General

Melting points were measured with a Mettler FP62 heating block. NMR spectra were recorded on a Bruker DMP

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Fig. 1. Formulae of the studied compounds.







III



IQ





IIQ

200 (¹H, ¹³C) spectrometer (reference Me₄Si, solvent CDCl₃). The IR and UV absorption spectra were respectively performed on a Perkin–Elmer Paragon 1000 PC and an Hitachi U-3300 spectrometers. Mass spectra were obtained using a VG Micromass Autospec Q instrument.

The chemicals were obtained from Aldrich and were used without further purification. The synthesized compounds were purified by column chromatography on silica gel 60 (70–200 mesh) using the appropriate eluents. The solid products were crystallized after chromatography.

2. Syntheses

2.1 Stilbene derivatives

4'-benzyloxy-2,5-dihydroxy-3,3'-dimethoxystilbene (I)

4'-benzyloxy-5-formyl-2-hydroxy-3,3'-dimethoxystilbene (3): Compounds 1 and 2 were prepared from vanillin by conventional methods respectively described in ref. 15 and 16. A *n*-butyl lithium solution in *n*-hexane (conc = $2.5 \text{ mol } \text{L}^{-1}$, 16 mmol) was added to a suspension of the phosphonium salt 2 (4.2 g, 8.0 mmol) in anhydrous THF (50 mL) under N₂ atmosphere and the mixture was stirred for 30 min at 0°C. The resulting red solution was treated with a solution of aldehyde 1 (1.6 g, 8.0 mmol) in anhydrous THF (40 mL). After being stirred for 3 h at room temperature, the THF was removed under vacuum, the residue was dissolved in CH₂Cl₂ and treated with hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated. The residue was purified by chromatography on silica gel (eluent: CH₂Cl₂-EP) affording the expected E stilbene 3 as white crystals (1.15 g, yield 37%, mp 133°C). IR (KBr) v: 950, 1010, 1080, 1140, 1260, 1520, 1600, 1690, 3400 cm⁻¹. ¹H NMR (CDCl₃) δ: 3.96 (s, 3H, OCH₃), 3.99 (s, 3H, OCH₃), 5.19 (s, 2H, OCH₂), 6.50 (s, 1H, OH), 6.88 (d, 1H, J = 8.24, $H_{5'}$), 7.04 (dd, 1H, J = 1.83and 8.24, $H_{6'}$, 7.13 (d,1H, J = 1.83, $H_{2'}$), 7.2–7.5 (m, 8H, ArH), 7.71 (d, 1H, J = 1.52 H₄ or H₆), 9.88 (s, 1H, CHO) ppm. ¹³C NMR (CDCl₃) δ: 56.1 (OCH₃), 56.4 (OCH₃), 71.0



(OCH₂), 106.9 (CH ar.), 109,6 (CH ar.), 113.9 (CH ar.), 114.6 (CH ar.), 119.7 (CH ar.), 120.1 (=CH), 124.1 (C ar.), 127.3 (CH Bn), 127.9 (CH Bn), 128.6 (CH Bn), 129.2 (C ar.), 130.6 (=CH), 130.8 (C ar.), 134.2 (C Bn), 147.3 (C ar.), 148.3 (C ar.), 148.6 (C ar.), 149.8 (C ar.), 191.2 (CHO) ppm.

4'-benzyloxy-2,5-dihydroxy-3,3'-dimethoxystilbene (I): A solution of compound 3 (600 mg, 1.4 mmol) in THF-water (30mL and 8 mL) under nitrogen atmosphere was treated with sodium carbonate (126 mg, 1.4 mmol) and oxygen peroxide (240 µL, 2.3 mmol). After being stirred at room temperature for 3 h, the reaction mixture was reacted with 1 mL of acetic acid. The aqueous layer was extracted with CH₂Cl₂ $(3 \times 30 \text{ mL})$. The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated. The residue was purified by crystallization (CH₂Cl₂-EP) affording the expected E stilbene I as white crystals (360 mg, yield 62%, mp 150°C). UV λ_{max} (MeOH)/nm : 320 (ϵ /L mol⁻¹ cm⁻¹ 19 600). IR (KBr) v : 960, 1000, 1080, 1130, 1260, 1510, 1600, 3400 cm⁻¹. ¹H NMR (CDCl₃) δ: 3.87 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃), 4.46 (s, 1H, OH), 5.14 (s, 2H, OCH₂), 5.55 (s, 1H, OH) 6.36 (d, 1H, H₄, J = 2.75 Hz), 6.60 (d, 1H, H₆, J = 2.75 Hz), 6.85 (d, 1H, H_{5'}, J = 8.22 Hz), 6.98 (dd, 1H, $H_{6'}$, J = 2.15 and 8.22 Hz), 7.00 (d, 1H, H_{α} or H_{α'}, J = 16.45 Hz), 7.11 (d, 1H, H_{γ'}, J = 2.15 Hz), 7.24 (d, 1H, H_{α} or $H_{\alpha'}$, J = 16.45 Hz), 7.25–7.6 (m, 5H, ArH) ppm. ¹³C ÑMR (CDCl₃) δ: 56.1 (OCH₃), 56.2 (OCH₃), 71.0 (OCH₂), 98.7 (CH ar.), 103.4 (CH ar.), 109.5 (CH ar.), 114.0 (CH ar.), 120.0 (CH ar.), 120.8 (=CH), 123.8 (C ar.), 127.3 (CH Bn), 127.9 (CH Bn), 128.6 (CH Bn), 129.3 (=CH), 137.1 (C Bn), 137.6 (C ar.), 147.3 (C ar.), 148.0 (C ar.), 148.7 (C ar.), 149.8 (C ar.) ppm. MS (EI) m/z (%): 378 (M^{+,} 65), 287 (100), 255 (14), 227 (14), 91 (48). HPLC-MS (solvent acetonitrile, negative mode) m/z: 377 (M – H)⁻.

2,5-diacetoxy-4'-benzyloxy-3,3'-dimethoxystilbene (III): Compound I (200 mg, 0.43 mmol) in dichloromethane (40 mL) was refluxed under nitrogen in presence of acetic anhydride (1.2 mL, 1.2 mmol), triethylamine (0.17 mL, 1.2 mmol), and 4-dimethylaminopyridine (DMAP, 5 mg) for 4 h. The reacting mixture was treated with hydrochloric acid (10%) and extracted with dichloromethane. The organic layer was washed with water to neutrality, dried over magnesium sulfate and evaporated under reduced pressure. The reacting mixture, separated by chromatography (eluent: CH₂Cl₂-Et₂O, 95:5), followed by crystallization in ethanol afforded the expected E stilbene III as white crystals (204 mg, yield 93%, mp 158°C). IR (KBr) v : 1030, 1080, 1140, 1180, 1210, 1270, 1510, 1590, 1760 cm⁻¹. UV λ_{max} (MeOH)/nm : 320 (ε/L mol⁻¹ cm⁻¹ 29 000). ¹H NMR (CDCl₃) δ: 2.31 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 3.81 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 5.18 (s, 2H, OCH₂), 6.66 (d, 1H, H_4 , J = 2.75 Hz), 6.87 (d, 1H, $H_{2'}$, J = 8.24 Hz), 6.91 (d, H_{α} , J = 15.26 Hz), 6.96–7.05 (m, 3H, H_6 , $H_{6'}$, and $H_{5'}$), 7.40 (d, $H_{\alpha'}$ J = 15.26 Hz), 7.3–7.5 (m, 5H, ArH) ppm. ¹³C NMR (CDCl₃) δ: 20.5 (CH₃), 21.2 (CH₃), 56.1 (OCH₃), 56.2 (OCH₃), 71.0 (OCH₂), 104.9 (CH ar.), 110.1 (CH ar.), 110.2 (CH ar.), 113.9 (CH ar.), 119.4 (CH ar.), 119.9 (=CH), 127.2 (CH Bn), 127.9 (CH Bn), 128.6 (CH Bn), 130.5 (C ar.), 131.8 (=CH), 131.9 (C ar.), 135.1 (C ar.), 137.0 (C Bn), 148.5 (C ar.), 148.7 (C ar.), 149.7 (C ar.), 168.7 (C=O), 168.8 (C=O) ppm. MS (EI) m/z (%): 462 (M⁺, 65), 432 (12), 371 (30), 329 (76), 299 (28), 287 (31), 255 (54), 227 (12), 91 (100), 43 (66).

(Z)-4'-benzyloxy-2,5-dihydroxy-3,3'-dimethoxystilbene (IZ): By irradiation with UV light ($\lambda \approx 350$ nm), compound I (50 mg, 0,13 mmol) in methanol (10 mL) solution degassed by bubbling nitrogen was converted to compound IZ ([IZ]:[I] = 90:10. The NMR data on IZ were obtained on the mixture after evaporation of the solvent and after subtracting the contribution of I. The electronic absorption spectrum of IQ was obtained with the diode array detector of the HPLC system (eluent: methanol). The mass spectrum of IQ was obtained using HPLC–MS technique with acetonitrile as eluent for the HPLC and electrospray for the ionization mode. UV λ_{max} (MeOH): 300 nm. ¹H NMR (CDCl₃) δ : 3.63 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), 5.09 (s, 3H, OCH₂), 6.27 (d, 1H, H₄, J = 2.44 Hz), 6.35 (d, 1H, H₆, J = 2.44 Hz), 6.55 (s, 2H, CH=CH), 6.76 (s, 1H), 6.77 (d, 1H, J = 1.83 Hz), 6.88 (d, 1H, J = 1.53 Hz), 7.25–7.45 (m, 5H, ArH) ppm. ¹³C NMR (CDCl₃) δ : 55.7 (OCH₃), 56.1 (OCH₃), 70.9 (OCH₂), 98.8 (CH ar.), 106.9 (CH), 112.2 (CH), 113.4 (CH), 122.0 (CH), 122.9 (CH), 123.3 (CH), 127.3 (CH Bn), 127.4 (CH Bn), 127.9 (CH Bn), 128.6 (C ar.), 129.3 (C ar.), 130.2 (C ar.), 130.7 (C ar.), 137.1 (C ar.), 137.3 (C ar.), 147.4 (C ar.), 148.4 (C ar.) ppm. HPLC–MS (solvent acetonitrile, negative mode); m/z: 377 (M – H)⁻.

2.2 Diphenyl ethane compounds

4'-benzyloxy-2,5-dihydroxy-3,3'-dimethoxydiphenylethane (II)

4'-benzyloxy-5-formyl-2-hydroxy-3,3'-dimethoxydiphenylethane (4): Hydrogenation of compound **3** (500 mg, 1.28 mmol) in ethyl acetate (100 mL) containing 50 mg of RhCl(PPh₃)₃ was accomplished by treating the mixture under hydrogen pressure (180 bar, 1 bar = 10^5 Pa) for 5 h at 80°C. The mixture, after filtration on a silica gel to removed the catalyst, afforded a white solid (500 mg, yield 100%). ¹H NMR (CDCl₃) δ : 2.9 (s, 4H, CH₂-CH₂), 3.8 (s, 3H, OCH₃), 3.9 (s, 3H, OCH₃), 5.0 (s, 2H, OCH₂), 6.5 (s, 1H, OH), 6.6–7.4 (m, 10H, ArH), 9.8 (s, 1H, CHO) ppm.

4'-benzyloxy-2,5-dihydroxy-3,3'-dimethoxydiphenylethane (II):

A solution of compound 4 (300 mg, 0.8 mmol) in a mixture of THF (20 mL)-water (5 mL) was treated with potassium carbonate (72 mg, 0.8 mmol) and hydrogen peroxide (150 µL, 1.4 mmol). After being stirred at room temperature for 1 h, the reaction was stopped by addition of 1 mL of acetic acid. The residue was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated under vacuum. The residue was purified by crystallization in a mixture of CH₂Cl₂-petroleum ether (1v:1v) affording the expected stilbene II as a white solid (200 mg, yield 70%, mp 119°C). UV λ_{max} (MeOH)/nm : 270 (ϵ/L mol⁻¹ cm⁻¹ 6800). IR (KBr) v: 730, 790, 1030, 1090, 1150, 1220, 1390, 1440, 1480, 1510, 2930, 3320 cm⁻¹. ¹H NMR (CDCl₃) δ : 2.86 (s, 4H, CH₂-CH₂), 3.85 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 4.80 (s, 1H, OH), 5.16 (s, 2H, OCH₂), 5.32 (s, 1H, OH), 6.17 (d, 1H, H_4 , J = 2.64 Hz), 6.34 (d, 1H, H_6 , J = 2.64 Hz), 6.72 (dd, 1H, $H_{6'}$, J = 1.95 and 8.10 Hz), 6.77 (d, 1H, $H_{2'}$, J = 1.95 Hz), 6.84 (d, 1H, H₅', J = 8.10 Hz), 7.30–7.55 (m, 5H, ArH) ppm. ¹³C NMR (CDCl₃) δ: 31.9 (CH₂), 35.4 (CH₂), 55.8 (OCH₃), 55.9 (OCH₃), 71.1 (OCH₂), 97.3 (CH ar.), 107.9 (CH ar.), 112.4 (CH ar.), 114.1 (CH ar.), 120.2 (CH ar.), 127.2 (CH Bn), 127.6 (CH Bn), 127.7 (C ar.), 128.4 (CH Bn), 135.4 (C ar.), 137.2 (C ar.), 137.3 (C ar.), 146.7 (C ar.), 148.3 (C ar.), 149.2 (C ar.) ppm. MS (EI) m/z (%): 380 (M^{+} , 30), 289 (35), 227 (40), 153 (33), 91 (100).

2,5-diacetoxy-4'-benzyloxy-3,3'-dimethoxydiphenylethane (IV): Hydrogenation of III (300 mg, 0.72 mmol) in ethyl acetate (50 mL) containing 30 mg of RhCl(PPh₃)₃ was accomplished by treating the mixture under hydrogen pressure (180 bar, 1 bar = 10⁵ Pa) for 5 h at 80°C. After filtration on silica gel, the solvent was removed under vacuum The compound IV was obtained as a white solid (300 mg, yield 100%, mp 130°C). UV λ_{max} (MeOH)/nm : 260 (ϵ /L mol⁻¹ cm⁻¹ 6900). IR (KBr) v : 1030, 1090, 1140, 1180, 1220, 1510, 1760, 2930 cm^{-1.} ¹H NMR (CDCl₃) δ: 2.28 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 2.78 (s, 4H, CH₂-CH₂), 3.80 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃), 5.14 (s, 2H, OCH₂), 6.54 (d, 1H, H₄, J = 2.75 Hz), 6.61 (d, 1H, H₆, J = 2.75 Hz), 6.65 (dd, 1H, H₆, J = 1.83 and 8.24 Hz), 6.69 (d, 1H, H₂, J = 1.83 Hz), 6.82 (d, 1H, H₅, J = 8.24 Hz), 7.25–7.50 (m, 5H, ArH) ppm. ¹³C NMR (CDCl₃) δ: 20.6 (OAc), 21.2 (OAc), 32.4 (CH₂), 35.6 (CH₂), 55.9 (OCH₃), 56.1 (OCH₃), 71.2 (OCH₂), 104.3 (CH ar.), 112.0 (CH ar.), 112.3 (CH ar.), 114.2 (CH ar.), 120.2 (CH ar.), 135.5 (C ar.), 135.7 (C ar.), 137.4 (C ar.), 146.5 (C ar.), 148.5 (C ar.), 149.5 (C ar.), 151.6 (C ar.), 168.9 (C=O), 169.4 (C=O) ppm. MS (EI): *m/z* (%): 464 (M⁺, 51), 422 (12), 380 (27), 331 (30), 289 (27), 257 (11), 227 (34), 195 (37), 183 (27), 137 (77), 91 (100), 43 (48).

Compound IV was also prepared in quantitative yield by acetylation of compound II using the procedure described for the synthesis of compound III.

2,5,4'-trihydroxy-3,3'-dimethoxydiphenylethane (6)

2,5-diacetoxy-4'-hydroxy-3,3'-dimethoxydiphenylethane (5): Hydrogenation of **III** (300 mg, 0.65 mmol) in anhydrous THF (50 mL) containing 30 mg of Pd–C was accomplished by treating the mixture under hydrogen pressure (80 bar, 1 bar = 10^5 Pa) for 24 h at 60°C. The mixture, after filtration on silica gel to removed the catalyst, afforded compound **5** (300 mg, yield 100%). ¹H NMR (CDCl₃) δ : 2.20 (s, 3H, OAc), 2.25 (s, 3H, OAc), 2.38 (s, 4H, CH₂-CH₂), 3.72 (s, 3H, OCH₃), 3.76 (s, 3H, OCH₃), 6.1–7.0 (m, 5H, ArH) ppm.

2,5,4'-trihydroxy-3,3'-dimethoxydiphenylethane (6): A solution of 5 (300 mg, 0.8 mmol) in methanol (25 mL) was treated with K₂CO₃ (350 mg, 4 mmol). After being stirred at 90°C for 4h, the solution was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with water, dried over MgSO₄, filtered, and concentrated. The reacting mixture was analyzed by ¹H NMR and by GC-MS after silulation. ¹H NMR (CDCl₃) δ : 2.20 (s, OAc), 2.41 (s, 4H, CH₂-CH₂), 3.75 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 6.0–7.0 (m, 5H, ArH) ppm. The observation of the peak at 2.20 ppm reveals the presence of compound 6Ac (50%) in addition to compound 6 (50%). This proportion was also revealed by GC-MS when the mixture was silvlated by treatment with pyridine (10 μ L), BSTFA (100 μ L) in dichloromethane. MS (EI) 6 silylated m/z (%): 433 ((M - 1)⁺, 33), 223 (14), 209 (100), 193 (11), 75 (12), 73 (34). MS (EI) 6Ac silvlated m/z (%): 476 (M^{+,} 14), 434 (57), 209 (100), 179 (15), 75 (13), 73 (41). This spectra indicates the incorporation of two trimethylsilyl groups in the molecule, the OH in the 2 position being too hindered to be substituted by the bulky TMS group.

2.3 Formation of p-quinonoid compounds

Quinone diphenylethane (IIQ)

Oxidation with $NaIO_4$: A solution of compound II (100 mg, 0.26 mmol) in a mixture of acetic acid (12 mL) – water (8 mL) was treated with sodium periodate (85 mg, 0.40 mmol). After being stirred at room temperature for 4h,

the organic layer was extracted with dichloromethane, dried over MgSO₄, and reduced under vacuum. The expected compound **IIQ** was obtained as a pale yellow oil (100 mg, yield 100%). IR (NaCl film) v : 2930, 1680, 1650, 1600, 1510, 1450, 1260, 1230, 1025, 790, 760 cm⁻¹. ¹H NMR (CDCl₃) δ : 2.75 (s, 4H, CH₂-CH₂), 3.82 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 5.13 (s, 3H, OCH₂), 5.88 (d, 1H, H₄, *J* = 2.44 Hz), 6.44 (d, 1H, H₆, *J* = 2.44 Hz), 6.65 (dd, 1H, H₆', *J* = 2.14 and 8.24 Hz), 6.73 (d, 1H, H₂', *J* = 2.14 Hz), 6.80 (d, 1H, H₅', *J* = 8.24 Hz), 7.2–7.5 (m, 5H, ArH) ppm.

Oxidation with Fremy's salt: A solution of compound II (100 mg, 0.26 mmol) in methanol (20 mL) was treated with Fremy's salt (KSO₃)₂NO (110 mg, 0.42 mmol) in water (5 mL) After being stirred at room temperature for 4h, the organic layer was extracted by dichloromethane, dried over MgSO₄, and reduced under vacuum. The expected compound **IIQ** was obtained as a pale yellow oil (100 mg, yield 100%).

Quinone stilbene (IQ): A solution of compound I (10 mg, 0.026 mmol) in acetonitrile was oxidized into quinone IQ by treatment under pressure of oxygen (20 bar, 1 bar = 10^5 Pa) at 60°C for 5 h. After evaporation of the solvent, the mixture was analyzed by HPLC and ¹H NMR. Products I and IQ were obtained in a 50:50 mixture. Various tentatives to isolate **IQ** as a pure compound by preparative chromatography were not successful due to the high reactivity of the quinone. So, the ¹H NMR spectrum of **IQ** was obtained from the reacting mixture spectrum by subtracting the contribution of compound I. The electronic absorption spectrum of IQ was obtained with the diode array detector on the HPLC system (eluent: methanol). The mass spectrum of IQ was obtained using HPLC-MS technique with acetonitrile as the eluent for the HPLC and electrospray for the ionization mode. This analysis did not allow the observation of the $(M - 1)^{-}$ peak as for I, but a peak was observed which corresponded to the addition of acetonitrile followed by the elimination of CO. UV λ_{max} (MeOH): 280 and 480 nm. ¹H NMR (CDCl₃) δ : 3.90 (s, 3H, OCH₃), 3.96 (s, 3H, OCH₃), 5.20 (s, 2H, OCH_2), 6.25 (d, 1H, H₄, J = 2.70 Hz), 6.55 (d, 1H, H₆, J = 2.70 Hz), 6.8–7.1 (4H, ArH and =CH), 7.25–7.6 (m, 6H, ArH and = CH) ppm. HPLC-MS (solvent acetonitrile, negative mode) m/z: 388 (M + CH₃CN-CO-H)⁻.

Quinone stilbene (IZQ): The stilbene quinone **IZQ** formed by irradiation of **I** in non-degassed solutions was characterized by HPLC equipped with a diode array detector (eluent: methanol) and HPLC–MS technique with acetonitrile as eluent for the HPLC and electrospray for the ionization mode. As for **IQ**, this analysis did not allow the observation of the (M – 1)⁻ peak, but a peak was observed which corresponds to the addition of acetonitrile followed by the elimination of CO. UV λ_{max} (MeOH): 270 and 470 nm. HPLC– MS (solvent acetonitrile, negative mode) m/z : 388 (M + CH₃CN–CO–H)⁻.

3. UV–Irradiation of models I, II, III and IV adsorbed on cellulose matrix

Four paper sheets $(3 \text{ cm} \times 3 \text{ cm})$ made from a kraft pulp (30 g/m^2) were separately impregnated with 2.0 mg of each compound in CH₂Cl₂ (1 mL) and dried with a nitrogen

stream. The paper sheets were irradiated with three black light UV lamps (Mazdafluor TFWN 18) emitting mainly in the 350 nm wavelength range. The distance between the lamp and the sheets was 20 cm. The temperature of the irradiation was maintained at 25° C by a fan. The reflectance of the sheets backed with a black and white backgrounds were measured at appropriate irradiation time intervals. The absorption (*K*) given by the Kubelka–Munk theory (17) was calculated and plotted as the difference between non irradiated and irradiated samples versus irradiation time.

4. Attempt to detect stilbene-hydroquinone chromophore in bleached mechanical pulp

Peroxide bleaching of mechanical pulp (BMP) and acetylation

Unbleached softwood mechanical pulp (20 g), kindly provided by Dr. Petit-Conil (Centre Technique du Papier, Grenoble), was treated in a polyethylene bag with the bleaching liquor (200 mL) constituted by hydrogen peroxide (3% oven dry pulp, odp), NaOH (1.5% odp), MgSO4·7H₂O (0.5% odp), sodium silicate (3.5% odp), and DTPA (0.25%) odp) at 60°C for 4 h. Then the pulp was filtered and bleached for a second time in the same conditions with fresh liquor (200 mL). At the end of the bleaching, the pulp was washed with distilled water and diluted hydrochloric acid to pH 4.5. Before acetylation, the pulp (1 g) was made alkaline by soaking it in a potassium carbonate solution (1 mol L^{-1}) for 15 min and filtrated under vacuum to remove the major part of the water. The pulp was then exposed to acetic anhydride vapor for 1 h and after was washed with water, ethanol and water to pH 4.5. At the end, the pulp was dried at 30°C for 24 h.

Hydrogenation of the acetylated BMP

Hydrogenation of the pulp (300 mg) impregnated with a solution of RhCl(PPh₃)₃ (15 mg) in ethyl acetate (3 mL) was accomplished under 180 bar (1 bar = 10^5 Pa) of hydrogen pressure for 4 h at 60°C in presence of 3 mL of ethyl acetate in the bottom of the reactor as described previously (14). After cooling the reactor, the pulp was washed with ethyl acetate, methanol, and CH₂Cl₂ to remove the catalyst and then washed with water and dried at 40°C for 24 h.

Thioacidolysis and Acidolysis with AlCl₃

100 mg of pulp were treated with 20 mL of thioacidolysis solution (10 mL EtSH + 2.4 mL BF₃–Et₂O + 80 mL dioxan) at 100°C for 4 h under gentle magnetic stirring. After hydrolysis with diluted NaHCO₃ solution until pH 3–4, the reaction mixture was extracted with dichloromethane. The organic phase was washed with water, dried over magnesium sulfate, and evaporated under vacuum. The residue was dissolved in benzene (30 mL) and was treated with 10 mg of AlCl₃ at 90°C for 12 h, then the reacting mixture was hydrolyzed with water and extracted with CH₂Cl₂. The organic phase was dried over magnesium sulfate concentrated under vacuum and silylated with BTSFA (50 μ L), pyridine (10 μ L) in THF (50 μ L) at room temperature. The silylated mixture was analyzed by GC–MS.

Fig. 2. Synthetic scheme of compounds I, II, III, and IV: (a) *n*-BuLi–DMF–THF; (b) 2, THF; (c) HCl 10%; (d) H_2O_2 –Na₂CO₃–THF–H₂O; (e) Ac₂O–NEt₃–DMAP–CH₂Cl₂; (f) H₂–Rh(PPh₃)₃Cl–ethyl acetate.



Results and discussion

1. Syntheses

The route chosen for the synthesis of compounds I, II, III, and IV is outlined in Fig. 2. The preparation of compound I which was similar to the Lee and Sumimoto (13) procedure, consists in the Wittig coupling between the ylide, generated by action of *n*-butyl lithium on the substituted benzyltriphenyl phosphonium chloride 1 (14), and the substituted salicylaldehyde 2 (16). The protection of the aldehyde group, needed for the coupling, was easily removed by treatment with hydrochloric acid at the end of the synthesis. Despite several attempts to improve the Wittig coupling e.g., by changing the reaction solvent, the yield was in our hands, lower (37%) than the one given by Lee (65%) (13) for the synthesis of a similar compound, but it was of the same order that we got for the syntheses of other lignin stilbene models (14). The hydroquinone **I** (*E* configuration) was obtained by Dakin reaction in mild conditions (room temperature and moderate pH given by the use of sodium carbonate). Compound **III** was synthesized in high yield (93%) by acetylation of compound **I**, using the catalytic action of 4-*N*,*N*-dimethylaminopyridine (DMAP) as for other lignin model compounds (18). Hydrogenation of compound **III**, was realized using experimental conditions set up previously for a study on the role of stilbenes issued from β -1 units on the photoyellowing of lignin rich pulps (14). Compound **II** which was prepared by catalytic hydrogenation of compound **3** followed by Dakin reaction at moderate pH, was quantitatively transformed into compound **IV** by acetylation.

Compound IZ was produced as a major product by irradiation of I in degassed methanol solution (Fig. 3). It was charFig. 3. Synthetic scheme of compounds IQ, IIQ, and IZ: (a) $P(O_2) = 20$ bar; (b) $NaIO_4$ -acetic acid-water; (c) $(KSO_3)_2NO$ -water.



Fig. 4. Synthetic scheme of compound 6: (a) H₂-Pd-C-THF; (b) K₂CO₃-methanol.



acterized by ¹H and ¹³C NMR and HPLC–MS (electrospray in the negative mode) spectroscopies (see experimental part).

In contrast to compound **II**, which gave the *p*-quinone **IIQ** by oxidation by sodium periodate or Fremy's salt, compound **I** did not produce the quinone **IQ** using the same reagents. The latter compound, very reactive and sensitive to chromatographic phases and eluents was obtained by oxidation of **I** in acetonitrile by oxygen under pressure (20 bar, 1 bar = 10^5 Pa) at 60°C (Fig. 3). The structure of **IQ** was determined by ¹H NMR and HPLC–MS (electrospray in the negative mode) spectroscopies (see experimental part). The structure of **IZQ** was assigned by comparison of its HPLC–UV spectrum and its HPLC–MS peaks with those of the quinone isomer **IQ** (see experimental part).

In order to characterize the presence of stilbene-hydroquinone chromophores in bleached pulps, compounds 5 and 6 were synthesized. Following a procedure previously used (14), and due to the high reactivity of the stilbene and hydroquinone units, the pulp was acetylated and hydrogenated prior to thioacidolysis and acidolysis with aluminum trichloride. The diphenylethane incorporating hydroquinone entities obtained from the pulp after the degradative treatment were expected to be in the form of their acetates or trimethylsilyl derivatives. The mild deacetylation procedure, very efficient for lignin models (18), and applied to compound **5**, produced a mixture of compounds **6** and **6Ac** (50%-50%). This mixture was silylated and used for the GC–MS analysis of the pulps, because it is likely that these two structures will be detected if the stilbene hydroquinone entities would be present in the peroxide bleached pulp. It is noticeable that silylation of compound **6** was incomplete, the OH in the 2 position being too hindered to react with the bulky trimethylsilyl group.

2. Electronic absorption and emission spectroscopies

Absorption spectra

The electronic absorption spectra of the stilbenes I, III and of the diphenylethanes II, IV are reported on Fig. 5.

The two diphenylethanes present a significant absorption above 300 nm, so they can absorb the solar light and so they can give colored species and contribute to the yellowing of peroxide-bleached high-yield pulps as already shown (19). The presence of the stilbene double bond increases the ab-

Fig. 5. Electronic absorption spectra of compounds I, II, III, and IV in methanol solutions (left) and of compound I in acidic and alkaline methanol solutions (right).



Fig. 6. Fluorescence emission spectra of compound I in ethanol solution. Left: neutral and acidic media; right: alkaline medium (λ_{exc} = 320 nm).





sorption above 300 nm compared to diphenylethanes, and so compound I which presents a very oxidizable phenol functional group, should be very sensitive to UV-irradiation. Moreover, phenols are in equilibrium with their phenolate anions and this equilibrium depends on the pH of the medium. In acidic or neutral media, the absorption of compound I is the same (Fig. 5). In contrast, in alkaline medium, compound I displays some absorption between 400 and 600 nm. The pulp industry usually produces papers with a basic reserve such as calcium carbonate for long term storage (20) but this alkaline treatment can induce a coloration of the materials if structures like compound I, which is ionized at pH 9, are present in lignin.

Fluorescence spectra

The interpretation of fluorescence spectra from wood, pulp, and paper samples is particularly cumbersome due to the physical heterogeneity and chemical complexity of the lignocellulosic matrix (21–23). Based on model studies (21, 22), it was shown that, in addition to cellulose emission, several chromophores of the lignin polymer are emitting in the region 330–430 nm. In contrast, the fluorophores at the origin of the emission of the pulp in the long wavelength range (430–530 nm) are still unknown. It is remarkable that the fluorescence emission, recorded for the stilbene **I** in neutral or acidic methanol solutions (Fig. 6), displays emission in this wavelength range (quantum yield ≈ 0.5 and lifetime ≈ 4 ns). This represents a bathochromic shift compared to other non-cyclic stilbene lignin models (22) and cyclic stilbene lignin model of the phenylcoumarone type (8*b*). In alkaline solution, the emission of compound **I** is shifted to longer wavelengths and its intensity is reduced, probably due to a highest reactive deactivation channel from the phenolate anion.

3. UV-irradiation of model I in solution

Compound I was irradiated in aerated methanol solutions (concentration $\approx 10^{-3}$ mol L⁻¹) with UV black lamps ($\lambda \approx 350$ nm). The irradiated solutions were analyzed by HPLC at different irradiaton times and some chromatogram traces are reported in Fig. 7.

The assignment of the HPLC peaks was carried out by comparison with samples analyzed by NMR and mass spectroFig. 7. HPLC analyses of photoproducts formed during irradiation of I in methanol.



scopies. The structure of the phenanthrene quinone derivative was assumed according to its UV absorption spectrum.

The UV absorption spectra of the photoproducts which were obtained with a diode array detector on the HPLC sys-

Fig. 9. Photoreactivity of compound I in solution.

Fig. 8. HPLC–UV analyses of photoproducts formed during irradiation of **I** in methanol. ⁰
⁰
Wavelength 250–700 nm
400 600



tem are drawn in Fig. 8. One can observe a hypsochromic shift (20 nm) for the absorption of the **IZ** isomer compared to the *E* isomer (this shift was already found by Stomberg et al. (24) on other lignin stilbene-like structures). Also a shift to the short wavelength (10 nm) is observed for the quinone IZQ compared to the *E* quinone **IQ**, both for $n\pi^*$ visible and for $\pi\pi^*$ UV transitions.

It is known that Z stilbenes are able to photocyclize to give phenanthrene derivatives (25). The dihydroxyphenanthrene formed by oxidative photocyclization of compound IZ might be transformed into p-phenanthrene quinone. The compound formed after 15 min of irradiation and having a retention time equal to 15 min might belong to this type of structure (Fig. 9). The photochemistry of compound I in methanol or acetonitrile solution is depicted in Fig. 9.



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Fig. 10. Irradiations of compounds adsorbed on cellulose paper. ΔK = absorption coefficient of irradiated paper – absorption coefficient of non irradiated paper. (*a*), (*b*), (*c*), (*d*): ΔK vs. λ for compounds **I**, **II**, **III**, and **IV** respectively.; (*e*) ΔK (425 nm) vs. irradiation time; (*f*) HPLC trace of extracted irradiated paper doped with compound **I**.



4. UV-irradiation of model I, II, III, and IV adsorbed on cellulose matrix.

The behavior of the lignin model compounds **I**, **II**, **III**, and **IV** adsorbed on cellulose paper were comparatively irradiated with UV light (see experimental part). The photocoloration was evaluated using the absorption coefficient given by the Kubelka–Munk theory (26). Fig. 10 (a–e) shows the difference of absorption coefficient (ΔK) of the lignin models adsorbed on cellulose paper before and after irradiation with UV light ($\lambda \approx 350$ nm) ranging from 5 min to 120 min. As observed for stilbenes formed from β -1 units (14), hydrogenated and acetylated chromophores display less variation of ΔK , which means less yellowing. The kinetics confirm the great reactivity of compound I. Its coloration is reduced by acetylation. Hydrogenation of compound I followed by acetylation leads to a very stable compound IV. In contrast, hydrogenation of I, which gives hydroquinone structure II, is not sufficient enough to stop the yellowing completely. The variations of ΔK observed for compound II is reminiscent to what was observed for 2methoxyhydroquinone in 2-hydropropylcellulose films (19).

After irradiation, the cellulose paper incorporating model **I** was extracted with solvent and analyzed by HPLC (Fig. 10*f*). Only the formation of quinone **IQ** is observed with no isomerization occurring. This is probably due the hydrogen bonding between the product and the cellulose

matrix which locks the configuration of the stilbene double bond. This confirms the key role of the environment in photochemical reactions.

5. Search for stilbene-hydroquinone chromophores in peroxide-bleached high-yield pulps

In order to assess and quantify the contribution of stilbene-hydroquinone chromophores in the photoreversion of high-yield pulps, we have attempted to find and quantify this structure in peroxide-bleached mechanical softwood pulp. For this purpose, we have used the same experimental procedure successfully set up for stilbenes emerging from β -1 lignin structures (14). In addition to the previous procedure, the pulp was first acetylated in the vapor phase in order to block the reactive hydroquinone groups. Even so, it was shown that catechol structures survive after the thioacidolysis (27). Therefore, after acetylation, hydrogenation, thioacidolysis with EtSH - BF₃-Et₂O in dioxane, and desulfurization with raney nickel, the organic residue was treated with AlCl₃ in benzene. The reacting mixture was analyzed by GC-MS. Careful inspection of the mass spectra of the chromatogram did not detect the silvlated compounds 6or 6Ac. So, it seems that a mechanical treatment is not strong enough to produce structures resembling compound I by mechanochemistry in high-yield pulps. However, we can never neglect that the chemical treatment, used to liberate the stilbene chromophore before analyses, is not efficient enough if the chromophore is situated in the bulk of the lignin polymer.

Conclusions

We studied stilbene-paraquinone models formed by mechanochemistry from β -5 units during grinding and disk-refining of pulp. The contribution of these structures to the photoyellowing of bleached high-yield pulps was evaluated examining the photochemistry of model I which was hydrogenated and (or) acetylated. Photoproducts formed during irradiation of compound I were characterized. In particular, the isomerization of compound I into IZ was found to be the main process in solution. In aerated solution, the stilbenes I and IZ were oxidized in paraquinones IQ and IZQ respectively. The isomerization of I was not observed when adsorbed on cellulose paper, only the formation of quinone IQ was obtained. Comparative irradiation of different models, adsorbed on thin sheets of cellulose paper, showed the greatest reactivity of model I. Hydrogenation coupled with acetylation produced an efficient stabilization of this compound. The detection and quantification of stilbene-hydroquinone units, present in peroxide-bleached mechanical pulp, could not be determined. This might be due to inefficient mechanochemistry in pulp, as suggested by Zhu's studies (28), or it might be due to inappropriate experimental conditions necessary to liberate the acetylated hydroquinone diphenylethane entities, these structures being characteristic of the stilbene–hydroquinone units formed from β -5 elements in lignin.

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