Attempt to approach the role of phenolic phenylpropenol structures in the photoyellowing of softwood mechanical pulps

Brigitte Ruffin, Stéphane Grelier, Aziz Nourmamode, and Alain Castellan

Abstract: Three biphenyl (**I**, **II**, **III**) compounds and a benzylarylether (**IV**) compound were synthesized to detect and quantify the presence of phenolic phenylpropenols in unbleached, peroxide-bleached, or sodium borohydride-reduced mechanical softwood pulps. The methodology used is based on a gas chromatography – mass spectrometry search of the prepared compounds in the residue obtained after ethylation, thioacidolysis, and desulfurization of the pulps. Detection of biphenyl **I** ($\approx 4 \times 10^{-6}$ mol g^{-1}) in unbleached and $NaBH_4$-reduced pulps is indicative of the presence of phenolic coniferaldehyde units in these pulps. Traces of biphenyl **II**, found in the peroxide-bleached pulp, probably came from ferulic acid units formed by oxidation of coniferaldehyde by H_2O_2. No biphenyl ether **III** or benzylaryl ether **IV** were detected in the three pulps. This result indicates that phenolic phenylpropenol units are not present in softwood mechanical pulps and do not contribute to the fast part of their photoyellowing.

Key words: mechanical pulp, photoyellowing, phenol, coniferyl alcohol, biphenyl.

Résumé : Trois biphenyls (**I**, **II**, **III**) et un éther benzylaryle (**IV**) ont été synthétisés afin de détecter et quantifier la présence de structures phénylpropénol dans des pâtes mécaniques de bois tendre non-blanchie, blanchie avec du peroxyde d'hydrogène ou réduite avec du borohydrure de sodium. La méthodologie utilisée est basée sur une recherche, par chromatographie – spectrométrie de masse, des composés préparés dans le résidu obtenu après éthylation, thioacidolyse et désulfuration des pâtes. La détection du biphényl **I** ($\approx 4 \times 10^{-6}$ mol g^{-1}) dans la pâte non-blanchie et dans celle réduite par $NaBH_4$ indique la présence de motifs coniféraldéhyde phénolique dans ces pâtes. Les traces du biphényl **II**, trouvées dans la pâte blanchie avec H_2O_2, proviennent vraisemblablement de structures acide férulique formées par oxydation par H_2O_2 d'unités coniféraldéhyde. L'absence de détection du biphényl **III** ou de l'éther benzylaryle dans les trois pâtes indique que les unités phénylpropénol phénolique ne sont pas présentes dans les pâtes mécaniques de bois tendre et ne contribue pas à la phase rapide de leur photojaunissement.

Mots clés : pâte à papier, lignine, photojaunissement, phénols, alcool coniférylique.

Introduction

High-yield pulps are obtained by the mechanical refining of wood. This defibration of lignocellulosic material might induce some chemical modification and new chemical structures might be formed. Phenylcoumaran and β-1 units are turned into stilbenes (1–3), β-*O*-4 entities are converted into *para*-hydroxybenzaldehydes (4), and coniferyl alcohols create α,β-unsaturated groups (5). Acidic treatment generates stilbenes (6) and phenylcoumarones, which are very sensitive to UV light (7, 8).

Comparison of the fluorescence emission between stoneground wood pulp and native wood (*abies* (fir)) (9) leads to the conclusion that pulp and wood behave similarly. Reduction of the material with sodium borohydride enhanced the fluorescence due to coniferyl alcohol and biphenyl units. It was observed that when paper and wood were subject to photobleaching of the fluorescent chromophores, the materials exhibited a photochromic effect (10). The borohydride-reduced woods performed differently in the photobleaching experiment from their paper counterpart. These subtle differences were attributed to stilbene chromophores formed by mechanochemistry present in paper and not in the wood (10). Nevertheless, studies on the effect of mechanical refining on the formation of photoactive chromophores in black spruce chips casts doubt on this effect (11).

When lignin-rich pulps are bleached with alkaline hydrogen peroxide, β-1 units are transformed into stilbenes (12), and α-carbonyl phenols and coniferaldehydes are converted into methoxyhydroquinones (13, 14). All these chromophores are considered to have a key role in the photoyellowing of bleached lignin-rich pulps (15). Lee and Sumimoto (16) considered that *para*-hydroxybenzoquinone derivatives, including stilbene-, biphenyl-, or diphenylether-conjugated structures, were the major ones responsible for color reversion of pulps. However, recent studies on light-induced brightness loss of pulps, which were targeted on the role of stilbene phenols formed from β-1 units (17) and stilbenes (including hydroquinone moieties formed from β-5 units (18)), indicate a minor role of these structural elements.

According to model studies (8, 19), phenolic coniferyl alcohol units were found to be very light-sensitive and might

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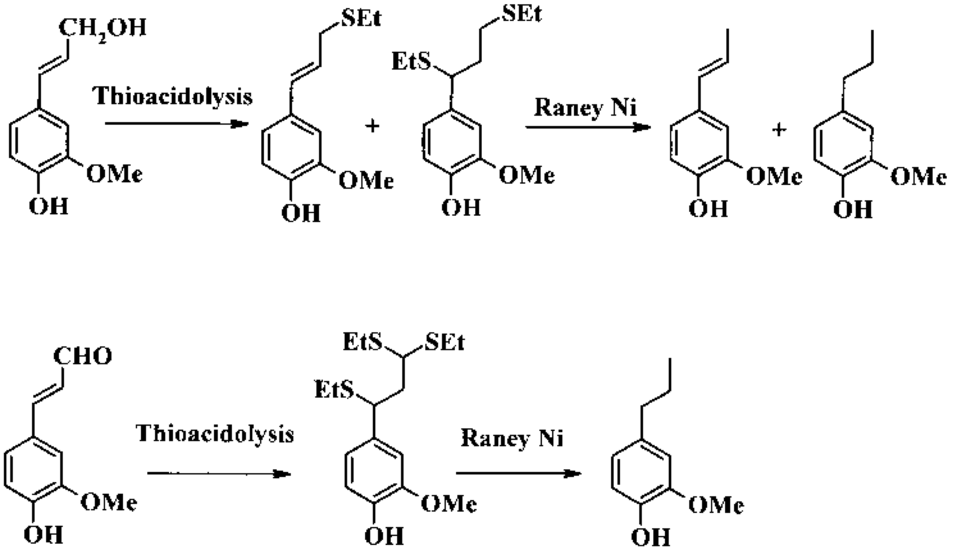
Fig. 1. Compounds obtained by thioacidolysis followed by desulfurization (Raney nickel) of coniferyl alcohol and coniferaldehyde (22, 24).



participate in the photoyellowing of bleached high-yield pulps. In our continuous effort to determine structures at the origin of the fast photoyellowing of lignocellulosic materials (17 to 18, 20 to 21), we present in this paper an attempt to detect, in pulp, the phenolic phenylpropenol moiety included in biphenyl or diarylether structures. The methodology used was thioacidolysis, followed by desulfurization with Raney nickel, GC–MS analysis, and comparison of the data with those from authentic samples synthesized for the purpose.

Results and discussion

General

During irradiation of thermomechanical pulps, Pan et al. (22) observed the formation of coniferyl aldehydes and the disappearance of coniferyl alcohols. Moreover, fluorescence studies on milled wood lignin (MWL) have revealed a great reactivity of coniferyl alcohol structures under irradiation (23); in particular, they are turned into coniferyl aldehydes and other structures that emit at 500 nm. It was observed that coniferyl aldehydes deactivate the emission at 400 nm caused by biphenyl structures. Based on this observation, we decided to attempt to detect and quantify phenolic phenylpropenols in high yield pulps and follow their evolution under UV–vis irradiation.

A widespread method for analysis and quantitative determination of lignin units is thioacidolysis; this method is a depolymerization of lignin by ethanethiol in the presence of $BF_3 \cdot Et_2O$, followed by gas chromatography separation and mass spectrometry analysis of the products (24). For analysis of lignin-condensed structures by thioacidolysis, a desulfurization step with Raney nickel is necessary, because condensed structures are too heavy to be analyzed by GC. However, reductive treatment leads to the formation of a propyl chain for both coniferyl alcohol and coniferyl aldehyde (Fig. 1) (24).

To differentiate phenolic coniferyl alcohol elements from non-phenolic coniferyl alcohol units, the pulp was ethylated. In this study, we looked for coniferyl alcohol structures included in the lignin macrostructure as biphenyl elements, such as structures **A** and **B**, and diarylether units, such as structure **C** (Fig. 2). Biphenyl structures were found to exist in high proportion in lignin in the form of dibenzodioxocin (25).

By thioacidolysis followed by desulfurization, structure **A** should lead to compounds **I–III** (Fig. 2). The same treatment applied on structure **B** should give compounds **I** and **III**. The syntheses of the biphenyl model compounds **I–III** and the diarylether model **IV** (representative of structure **C**) (Fig. 2) were completed. Compound **V**, isomer of **III**, was not considered because it is not formed from structure **B**, and unit **A** is accounted for by dimers **I–III**. The investigation was made on three pulps: unbleached mechanical softwood pulp (MSP) (mainly from spruce), hydrogen peroxide bleached MSP, and sodium borohydride reduced MSP (vide infra).

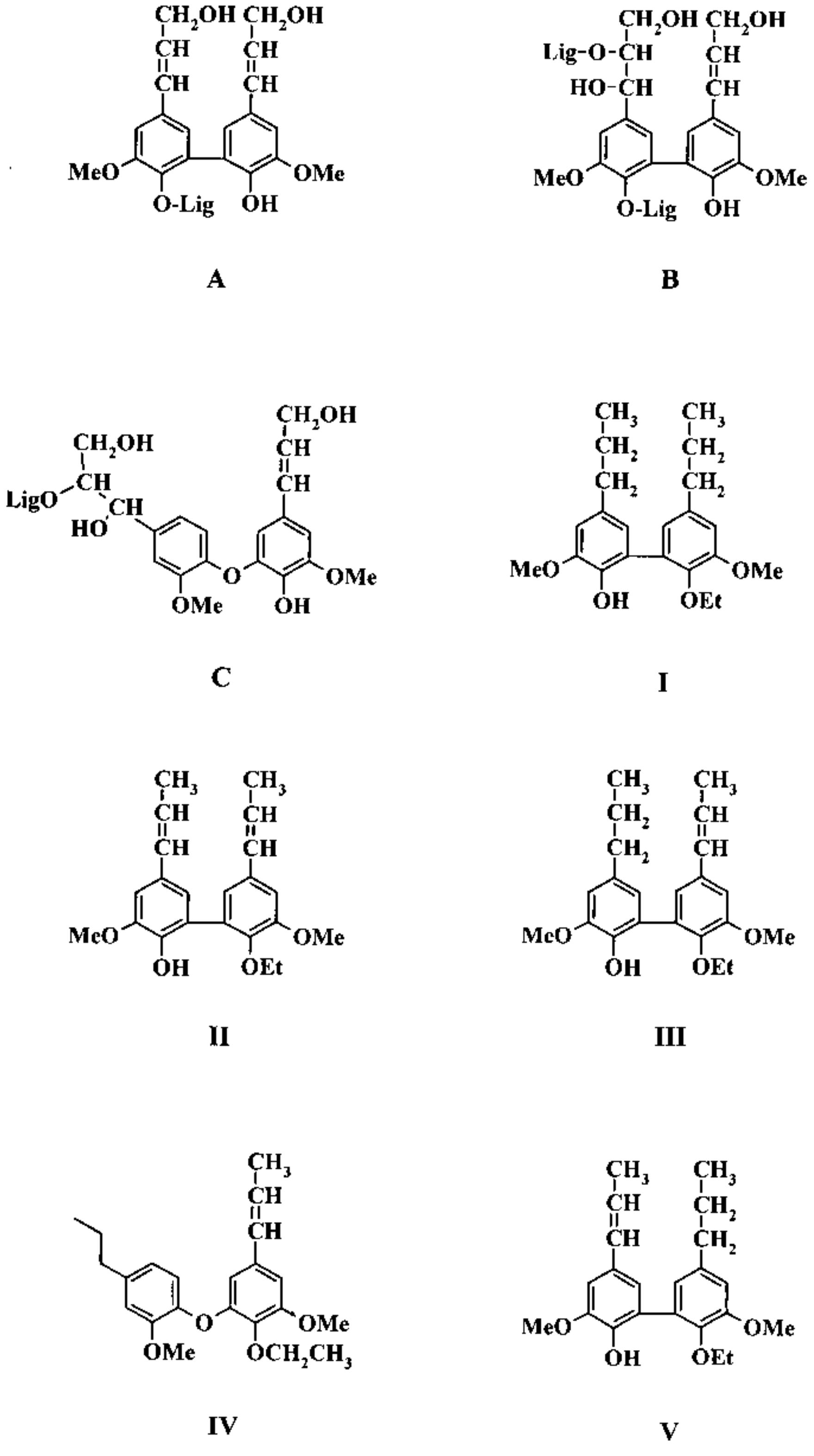
Synthesis of compounds

Synthesis of compound **I** is described in Fig. 3. The key step in this synthesis is the monoprotection of one of the two phenoxyl groups of the biphenyl. Eugenol is converted into the dehydrodimer by oxidative coupling with potassium ferricyanide. The compound obtained is then hydrogenated and monoethylated by treatment with diethylsulfate with sodium hydroxide, thanks to the different acidity between the two phenolic groups (26).

Compound **II** could not be obtained by isomerization of the corresponding isomer at high temperature (unlike isoeugenol, which is obtained from eugenol by treatment with sodium hydroxide in diethylene glycol (27)). Other attempts with different solvents (DMSO, THF) or bases (*t*-BuOK) were conducted without success. Compound **II** was prepared according to the route described in Fig. 4. GC–MS analysis of compound **II** revealed the presence of four propene chain isomers in the relative ratio 36:30:19:15. According to their relative stability, the highest and lowest figures could be assigned to *E*,*E* and *Z*,*Z* isomers.

Compound **III** was synthesized according to the scheme described in Fig. 5. The key step for this synthesis is the Kharasch reaction between a Grignard reagent and an aryl halide (28, 29).

Fig. 2. Phenolic phenylpropenol units present in softwood pulp and structures resulting from thioacidolysis and desulfurization treatments.



Compound **IV** was obtained by the reaction sequence described in Fig. 6. The yield (3.5%) is very low because the main product formed by this procedure was compound **2**. The latter is formed by oxidative coupling of compound **10** in the presence of Cu^{2+} (30).

Analysis of the pulps

To characterize only phenolic coniferyl alcohol structures, the pulp was treated with diethylsulfate in alkaline medium — this is a very efficient reaction to etherify phenols. Then the pulps were thioacidolysed and desulfurized. GC–MS

Fig. 3. Synthetic scheme of compound **I**.

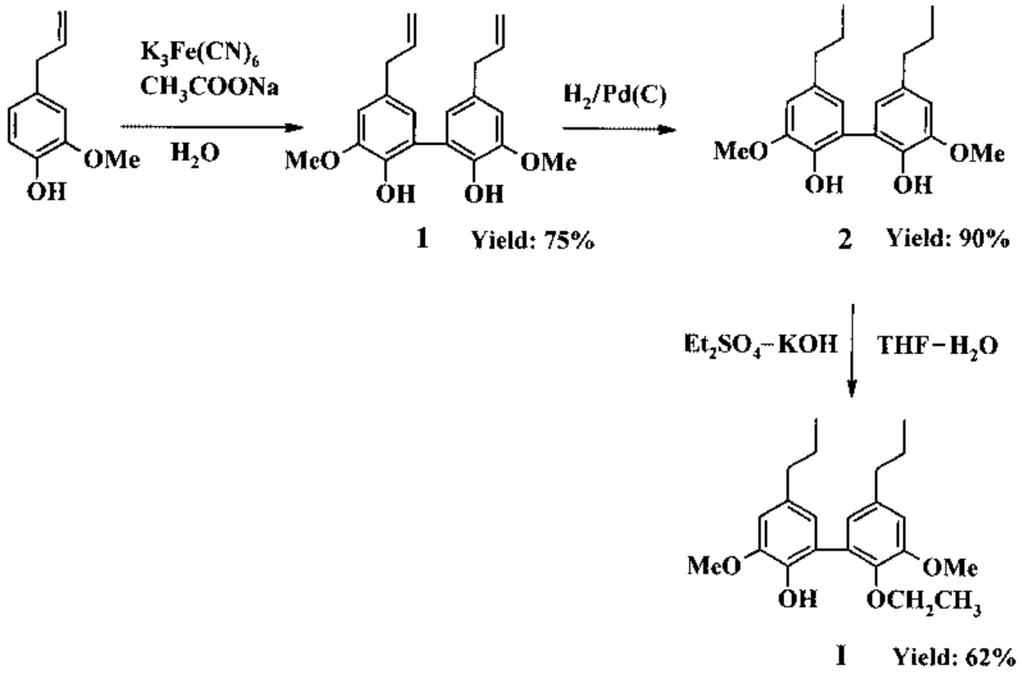
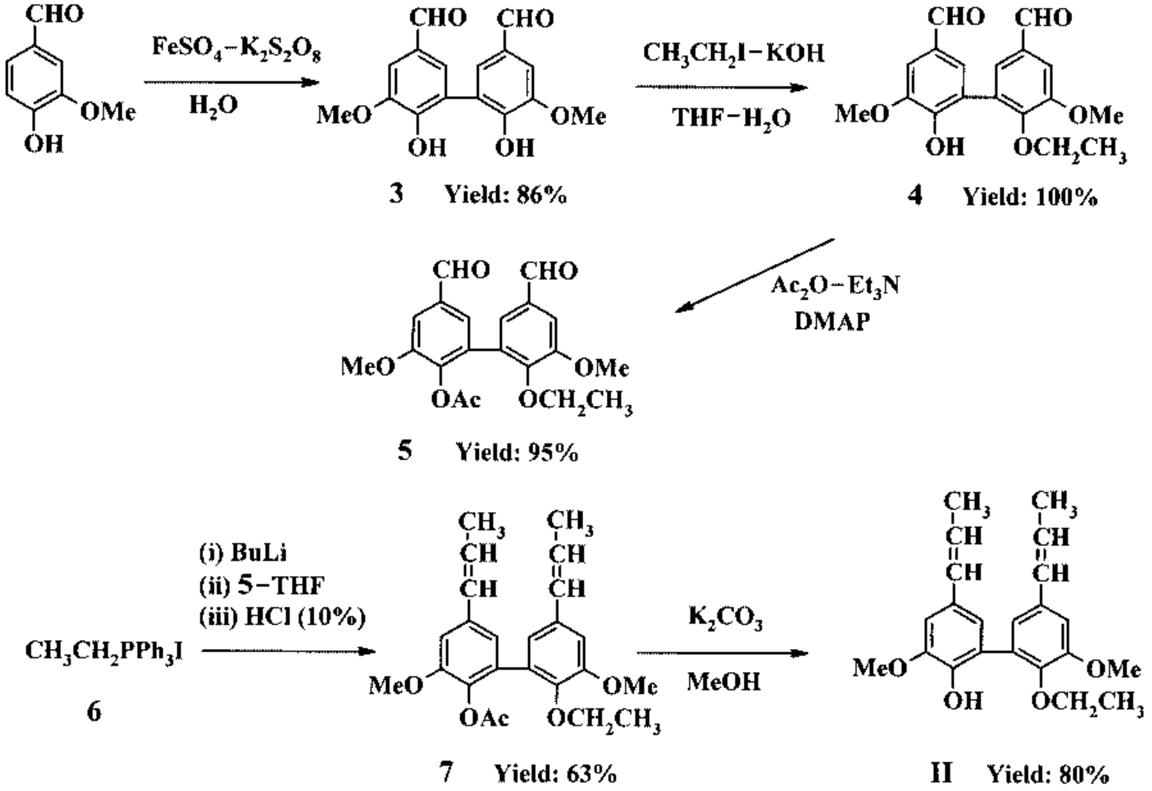


Fig. 4. Synthetic scheme of compound **II**.



analyses are reported in Table 1 for unbleached and H_2O_2- and $NaBH_4$-treated pulps.

Among the four studied compounds, only compound **I** was found in unbleached and reduced pulps, in minute quantity ($\approx 4 \times 10^{-6}$ mol g^{-1}), which represents an order of magnitude higher than that found for stilbene phenols in peroxide bleached pulps (17). In peroxide bleached pulp, compound **I** was not detected. It is likely that compound **I** is not formed from phenylpropenol units but from phenylpropenal ones, these structures being degraded by hydrogen peroxide.

Fig. 5. Synthetic scheme of compound **III**.

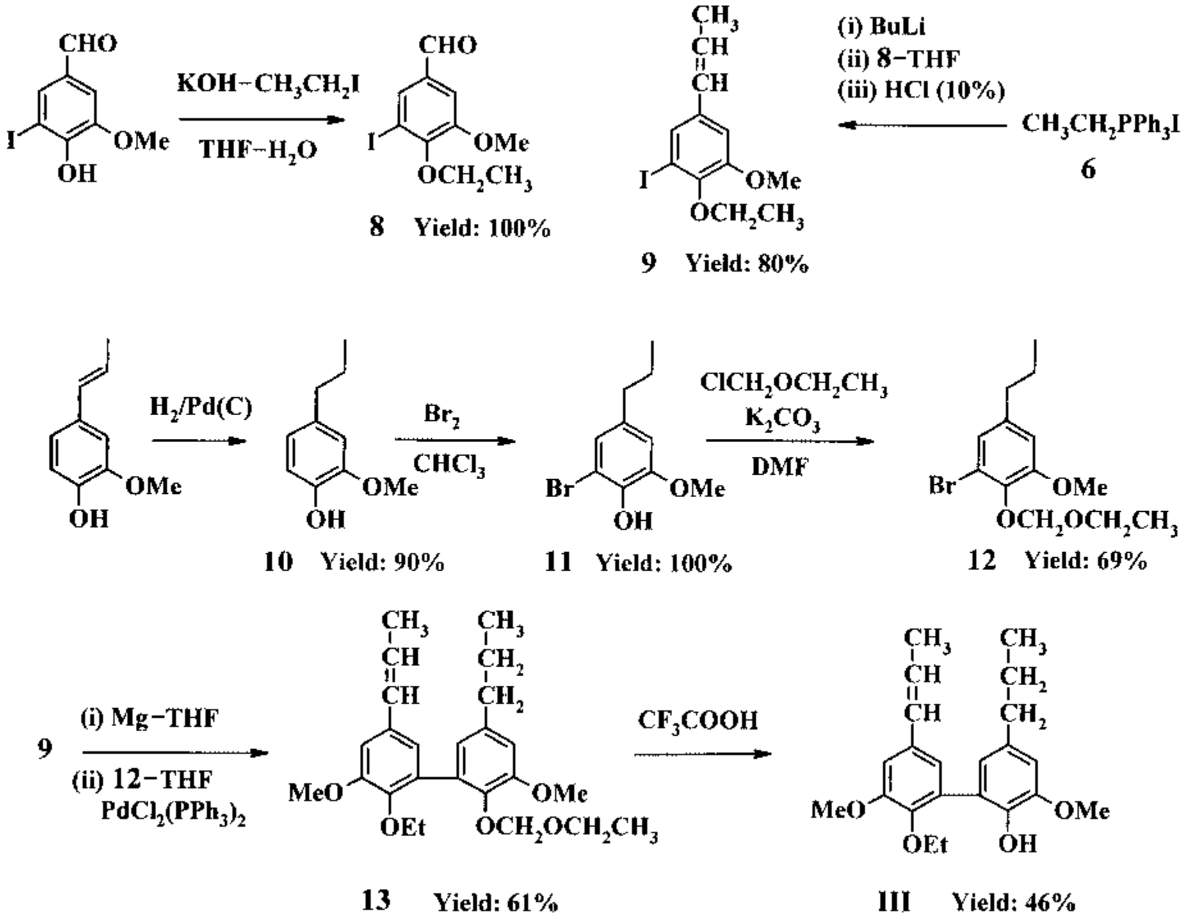
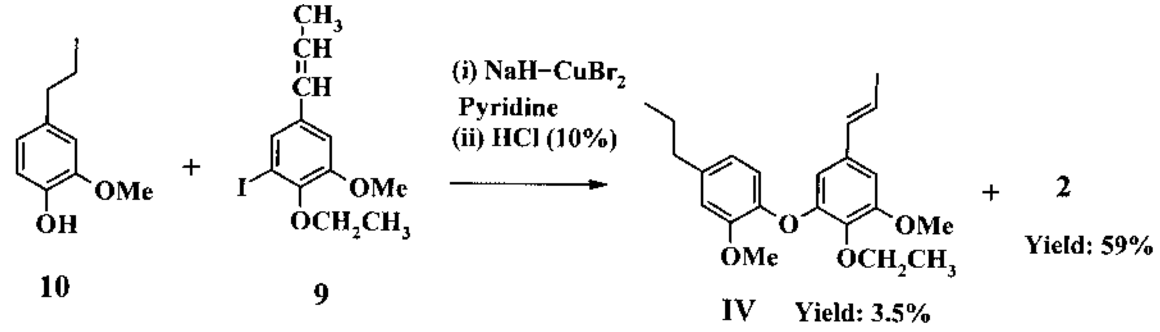


Fig. 6. Synthetic scheme of compound **IV**.



Traces of compound **II** were detected only for peroxide treated pulp in the form of two isomers, *E,E* and *Z,E* or *E,Z*. These isomers might be formed from cinnamic acid structures generated by the action of hydrogen peroxide on coniferaldehyde units. The lack of detection of compounds **III** and **IV** would indicate a very low content of phenolic coniferyl alcohol units or an inefficient ethylation of phenols, which is improbable considering the detection of compound **I** and the large excess of diethylsulfate used to treat pulps.

The lack of detection of compounds **III** and **IV** indicates that phenolic phenylpropenol units are not present in large amounts in bleached softwood mechanical pulps and therefore do not contribute to their fast photoyellowing.

Experimental

General

Melting points were measured with a Mettler FP62 heating block. NMR spectra were recorded on a Bruker DPX200 (^{1}H, ^{13}C) spectrometer (reference Me_4Si, solvent $CDCl_3$). The IR and UV absorption spectra were performed on PerkinElmer Paragon 1000 PC and Hitachi U-3300 spectrometers, respectively. Mass spectra were obtained using a VG Micromass Autospec Q instrument incorporating an electron ionization source (70 eV).

The usual chemicals were obtained from Aldrich, and they were used without further purification. The synthesized compounds were purified by column chromatography on

Table 1. Detection and quantification by GC–MS of compounds **I**, **II**, **III**, and **IV** in softwood mechanical pulps after thioacidolysis and desulfurization.

Pulp and (or) compounds (1×10^{-6} mol g^{-1})	I	II	III	IV
Untreated pulp	3.7	n.d.	n.d.	n.d.
H_2O_2-bleached pulp	—	Trace of two isomers	n.d.	n.d.
$NaBH_4$-reduced pulp	4.5	n.d.	n.d.	n.d.

Note: n.d. = not detected

silica gel 60 (70–200 mesh) using the appropriate eluents. The solid products were crystallized after chromatography.

Analysis of the compounds was performed by gas chromatography (GC) with a flame ionization detector (Shimadzu GC 14A equipped with a CR4A Chromatopac data analyzer) or GC (Hewlett-Packard 5890 chromatograph) interfaced with a mass spectrometer (VG Micromass Autospec Q). The GC analyses were made using capillary columns (J and W Scientific) (30 m × 0.25 mm; film thickness, 0.25 μm; stationary phase DB-5MS). The injector port temperature was set at 280°C and the detector port temperature at 300°C (Shimadzu GC 14A). The transfer line between the GC apparatus and the mass spectrometer source was fixed at 220°C. The oven temperature program (GC) started at 180°C (1 min), then rose between 180 and 300°C with a gradient of 4°C min^{-1}, and finally was set to 300°C (30 min).

Chemical treatment of pulp

Bleaching of pulp with hydrogen peroxide

Mechanical pulp, mainly from spruce (0.5 g), kindly given by Dr. Petit-Conil (Centre Technique du Papier, Grenoble, France), was treated with hydrogen peroxide (30%, 0.5 mL) and sodium hydroxide (10 mg in 50 mL of water) in a plastic bag. After being heated at 50°C for 4 h, the pulp was washed with distilled water, diluted hydrochloric acid (5%), and water to bring the pH near 5. The pulp was filtered and keep at 4°C before etherification with diethylsulfate.

Reduction of pulp with $NaBH_4$

Mechanical pulp mainly from spruce (0.5 g) was reacted with sodium borohydride (0.5 g in 20 mL of water). After being stirred at room temperature for 2 days, the pulp was washed with hydrochloric acid (5%) and water to bring the pH near 5. The pulp was filtered and kept at 4°C before etherification with diethylsulfate.

Ethylation of pulps

The defiberized pulps (3 g) in suspension in water (100 mL) were treated under magnetic stirring and a nitrogen atmosphere with 5 mL of 10% sodium hydroxide solution. The mixtures were heated at 40°C for 15 min and then diethylsulfate (2 mL) was added. The stirring was continued for 1 h and then the alternating addition of sodium hydroxide and diethylsulfate was repeated. This cycle was repeated once more. Then the pulp was successively washed with dilute hydrochloric acid (5%) and distilled water (to pH ≈ 5), and filtered. The pulp was first dried in an oven at 40°C and then over P_2O_5 under vacuum before thioacidolysis treatment.

Thioacidolysis and Raney nickel treatment of pulps

Thioacidolysis and desulfurization experiments were performed according to a procedure described by Lapierre et al. (24, 31). Pulp (50 mg), treated with 10 mL of thioacidolysis solution (10 mL EtSH + 2.4 mL $BF_3 \cdot Et_2O$ + 80 mL dioxan), was heated at 100°C for 4 h under magnetic stirring. After hydrolysis with diluted $NaHCO_3$ solution until pH 3 to 4, the reaction mixture was extracted with dichloromethane. To the dichloromethane solution, docosane was added as an internal standard for quantitative measurements. The organic phase was washed with water, dried over magnesium sulfate, and evaporated under vacuum. The solid residue was dissolved in 0.5 mL of dichloromethane and reacted with 2 mL of aqueous Raney nickel solution (50%) in 10 mL of methanol for 4 h at 80°C. After cooling, the resulting mixture was hydrolyzed with hydrochloric acid (10%) and extracted with dichloromethane. The organic phase, after washing with water, was dried over magnesium sulfate and evaporated to 0.5 mL. The organic phase was silylated with BSTFA (50 μL) in the presence of pyridine (10 μL) at room temperature for 30 min.

Syntheses

Synthesis of compound I

*5,5′-Diallyl-2,2′-dihydroxy-3,3′-dimethoxybiphenyl (dihydrodiisoeugenol) (**1**)*

A solution of eugenol (5.0 g, 30.5 mmol) and sodium acetate (9.0 g, 110.0 mmol) in water (200 mL) was treated, dropwise, with a solution of potassium ferricyanide (20.0 g, 60.8 mmol) in water (200 mL). After being stirred at room temperature for 3 h, the reaction mixture was filtered and the solid product was purified by crystallization in CH_2Cl_2 – petroleum ether (PET), affording the expected biphenyl **1** as beige crystals (3.8 g), yield 75%; mp 107°C (lit. (32) value mp +106°C). ^{1}H NMR ($CDCl_3$) δ: 3.40 (d, 4H, CH_2), 3.84 (s, 6H, OCH_3), 5.17 (d, 4H, =CH_2), 6.0 (m, 4H, CH), 6.9–7.0 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 40.0 (CH_2), 56.1 (OCH_3), 110.7 (CH Ar), 115.7 (=CH_2), 123.1 (CH Ar), 124.3 (C Ar), 131.9 (C Ar), 137.7 (=CH), 140.9 (C Ar), 147.2 (C Ar).

*2,2′-Dihydroxy-3,3′-dimethoxy-5,5′-di-*n*-propylbiphenyl (**2**)*

Hydrogenation of compound **1** (2.0 g, 6.1 mmol) in methanol (75 mL) containing 0.2 g of carbon palladium (10%) was accomplished by treating the mixture under hydrogen pressure (180 bar) for 24 h at room temperature. The mixture, after filtration, afforded a beige solid (1.8 g, 90%); mp 152°C (lit. (33) value mp +152°C). IR (KBr) (cm^{-1}): 850, 1050, 1145, 1230, 1260, 1375, 1425, 2920, 2945, 3300. ^{1}H NMR ($CDCl_3$) δ: 0.95 (t, 6H, CH_3), 1.63 (m, 4H, CH_2), 2.55 (t, 4H, CH_2), 3.91 (s, 6H, OCH_3), 6.03 (s, 2H, OH), 6.7

(m, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 13.9 (CH_3), 24.8 (CH_2), 37.9 (CH_2), 56.1 (OCH_3), 110.6 (CH Ar), 122.9 (CH Ar), 124.4 (C Ar), 134.7 (C Ar), 140.5 (C Ar), 147.1 (C Ar).

*2-Hydroxy-2′-ethoxy-3,3′-dimethoxy-5,5′-di-*n*-propylbiphenyl (**I**)*

A solution of compound **2** (600 mg, 1.82 mmol) in THF (50 mL) was treated with a solution of potassium hydroxide (102 mg, 1.82 mmol) and diethylsulfate (0.5 mL, 4.0 mmol). After being stirred at 70°C for 12 h, the solution was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated. The product was purified by chromatography on silica gel (eluent Et_2O–PET, 60:40) affording the expected compound **I** (400 mg, 62%) as a pale yellow oil. IR (NaCl) (cm^{-1}): 840, 1050, 1140, 1230, 1460, 1580, 2870, 2930, 2960. ^1H NMR ($CDCl_3$) δ: 0.84 (t, 3H, CH_3), 0.86 (t, 3H, CH_3), 1.02 (t, 3H, CH_3), 1.55 (m, 4H, 2×CH_2), 2.46 (t, 2H, CH_2), 2.48 (t, 2H, CH_2) 3.74 (q, 2H, OCH_2), 3.78 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.6–6.7 (m, 4H, ArH), 6.72 (s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ: 13.8 (CH_3), 14.0 (CH_3), 15.3 (CH_3), 24.6 (CH_2), 24.8 (CH_2), 37.8 (CH_2), 38.0 (CH_2), 55.9 (OCH_3), 56.1 (OCH_3), 69.9 (OCH_2), 111.2 (CH Ar), 111.7 (CH Ar), 122.9 (CH Ar), 123.4 (CH Ar), 128.2 (C Ar), 132.6 (C Ar), 134.3 (C Ar), 139.2 (C Ar), 141.2 (C Ar), 142.4 (C Ar), 148.5 (C Ar), 152.6 (C Ar). MS (TMS derivative): 430 ($[M]^{+\cdot}$,100%), 401 (10%), 387 (14%), 357 (9%), 73 (31%).

Synthesis of compound II

*4,4′-Diformyl-2,2′-dihydroxy-3,3′-dimethoxybiphenyl (**3**)*

Vanillin (5.0 g, 33 mmol) in hot water (200 mL) was treated by ferrous sulfate (200 mg, 0.7 mmol) and potassium persulfate (5.0 g, 20 mmol) at 100°C for 2 h. The resulting product was filtered and dried in an oven, affording the expected compound **3** (4.3 g, 86%); mp 304°C (lit. (34) value mp +305°C). IR (KBr) (cm^{-1}): 750, 850, 1050, 1150, 1260, 1420, 1460, 1590, 1680, 3260. ^1H NMR (DMSO) δ: 3.98 (s, 6H, OCH_3), 7.4 (s, 4H, ArH), 9.85 (s, 2H, CHO). ^{13}C NMR (DMSO) δ: 56.0 (OCH_3), 109.0 (CH Ar), 124.5 (CH Ar), 127.9 (C Ar), 128.2 (C Ar), 148.1 (C Ar), 150.3 (C Ar), 191.1 (CHO).

*2-Ethoxy-4,4′-diformyl-2′-hydroxy-3,3′-dimethoxybiphenyl (**4**)*

Dehydrodivanillin **3** (3.0 g, 9.9 mmol) in THF (100 mL) was treated with a solution of potassium hydroxide (0.6 g, 10.0 mmol) in water (10 mL) and iodoethane (3.2 g, 20.5 mmol). After being refluxed for 6 h, the mixture was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated, affording the expected compound **4** (3.3 g, 100%) as a pale yellow solid; mp 195°C. IR (KBr) (cm^{-1}): 740, 890, 1040, 1150, 1180, 1260, 1420, 1580, 1700, 3250. ^1H NMR ($CDCl_3$) δ: 1.11 (t, 3H, CH_3), 3.98 (s, 3H, OCH_3), 4.01 (q, 2H, OCH_2), 4.06 (s, 3H, OCH_3), 6.59 (s, 1H, OH), 7.4–7.5 (m, 4H, ArH), 9.86 (s, 1H, CHO), 9.92 (s, 1H, CHO).

*2-Ethoxy-4,4′-diformyl-2′-acetoxy-3,3′-dimethoxybiphenyl (**5**)*

A solution of **4** (3.3 g, 9.9 mmol) in CH_2Cl_2 (50 mL) was treated with triethylamine (5 mL, 36.1 mmol), acetic anhydride (1.4 mL, 12.6 mmol), and traces of 4-dimethylaminopyridine (DMAP). After being refluxed for 20 h, the mixture was reacted with water. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated, affording the expected compound **5** (3.5 g), yield 95%, as a pale yellow solid; mp 127°C. IR (KBr) (cm^{-1}): 740, 890, 1040, 1130, 1180, 1270, 1380, 1576, 1700, 1765. ^1H NMR ($CDCl_3$) δ: 1.08 (t, 3H, CH_3), 2.10 (s, 3H, OAc), 3.92 (q, 2H, OCH_2), 3.94 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 7.2–7.5 (m, 4H, ArH), 9.87 (s, 1H, CHO), 9.95 (s, 1H, CHO).

*Ethyltriphenylphosphonium iodide (**6**)*

A solution of iodoethane (3.0 g, 19.1 mmol) in toluene (50 mL) was treated with triphenylphosphine (6.0 g, 23.0 mmol) at 80°C for 3 h. The resulting white product was filtered and dried, affording the expected salt **6** (6.8 g), yield 84%; mp 168°C (lit. (35) value mp +168 to 169°C).

*2-Ethoxy-4,4′-diformyl-2′-acetoxy-3,3′-dipropenylbiphenyl (**7**)*

An *n*-butyl lithium solution in *n*-hexane (2.5 mol L^{-1}, 5.2 mmol) was added to a solution of the phosphonium salt **6** (2.1 g, 5 mmol) in anhyd THF (30 mL) under an N_2 atmosphere and the mixture was stirred at –70°C for 15 min. The resulting red solution was treated with a solution of aldehyde **5** (0.9 g, 2.4 mmol) in anhyd THF (20 mL). After being stirred at room temperature for 2 h, the mixture was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated. The product was purified by chromatography on silica gel (eluent CH_2Cl_2) affording the expected compound **7** (0.6 g, 63%) as a yellow solid; mp 127°C. IR (KBr) (cm^{-1}): 760, 790, 960, 1050, 1140, 1460, 1580, 1700, 1770, 2950. ^1H NMR ($CDCl_3$) δ: 1.1 (t, 3H, CH_3), 1.6 (2d, 6H, CH_3), 2.0 (s, 3H, OAc), 3.9 (m, 8H, 2 × OCH_3 and OCH_2), 5.5–6.0 (m, 4H, CH=CH), 6.8 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 15.4 (CH_3), 20.4 (Ac), 56.0 (OCH_3), 56.3 (OCH_3), 69.6 (OCH_2), 109.7 (CH Ar), 110.1 (CH Ar), 127.1 (CH Ar), 127.4 (CH Ar), 130.7 (C Ar), 132,0 (C Ar), 132.5 (C Ar), 134.3 (C Ar), 190.8 (CHO), 191.0 (CHO).

*2-Ethoxy-4,4′-diformyl-2′-hydroxy-3,3′-dipropenylbiphenyl (**II**)*

A solution of **7** (600 g, 1.52 mmol) in methanol (50 mL) was treated with potassium carbonate (250 mg, 1.81 mmol). After being stirred at room temperature for 4 h, the mixture was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated. The product was purified by chromatography on silica gel (eluent CH_2Cl_2–Et_2O, 98:2) affording the expected compound **II** (450 mg, 80%) as a pale yellow oil; mp 127°C. ^1H NMR ($CDCl_3$) δ: 1.1 (t, 3H, CH_3), 1.8 (d, 3H, CH_3), 1.9 (d, 3H, CH_3), 3.9 (m, 8H, 2 × OCH_3 and OCH_2), 5.6–7.0 (m, 8H, ArH, and CH=CH). Four stereoisomers displaying the same mass spectrum were identified by GC–MS (retention time: 18.8 (30%), 19.7 (36%), 20.0 (15%), and 21.0 min (19%)). MS (TMS derivative): 426 ($[M]^+$, 100%), 383 (12%), 73 (35%).

Synthesis of compound III

4-Ethoxy-5-iodo-3-methoxybenzaldehyde (8)

5-Iodovanillin (3.0 g, 10.8 mmol) in THF (75 mL) was treated with a solution of potassium hydroxide (1.0 g, 17.8 mmol) in water (10 mL) and iodoethane (4.0 g, 25.6 mmol). After being refluxed for 6 h, the mixture was reacted with water. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with a solution of hydrochloric acid (10%), dried over $MgSO_4$, filtered, and concentrated, affording the expected compound **8** (3.3 g, 100%) as white crystals; mp 42°C. IR (KBr) (cm^{-1}): 590, 670, 790, 1040, 1150, 1270, 1390, 1460, 1560, 1580, 1690, 2970. ^1H NMR ($CDCl_3$) δ: 1.25 (t, 3H, CH_3), 3.83 (s, 3H, OCH_3), 4.05 (q, 2H, OCH_2), 7.23 (d, 1H, ArH), 7.77 (d, 1H, ArH), 9.81 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$) δ: 15.7 (CH_3), 56.2 (OCH_2), 69.5 (OCH_3), 110.0 (CH Ar), 118.3 (C-I), 128.6 (CH Ar), 132.8 (C Ar), 151.0 (C Ar), 154.2 (C Ar), 169.9 (CHO).

2-Ethoxy-1-iodo-3-methoxy-5-propenylbenzene (9)

An *n*-butyl lithium solution in *n*-hexane (2.5 mol L^{-1}, 10.0 mmol) was added to a solution of the phosphonium salt **6** (4.2 g, 10.0 mmol) in anhyd THF (50 mL) under N_2 atmosphere and the mixture was stirred at –70°C for 15 min. The resulting red solution was treated with a solution of aldehyde **8** (3.0 g, 9.8 mmol) in anhyd THF (40 mL). After being stirred at room temperature for 2 h, the mixture was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated. The product was purified by chromatography on silica gel (eluent CH_2Cl_2) affording the expected compound **9** (2.5 g), yield 80%, as a pale yellow solid; mp 33°C. IR (KBr) (cm^{-1}): 780, 870, 960, 1050, 1140, 1230, 1250, 1510, 2950. ^1H NMR ($CDCl_3$) δ: 1.44 (t, 3H, CH_2-CH_3), 1.87 (2 × dd, 3H, CH-CH_3), 3.85 (s, 3H, OCH_3), 4.04 (q, 2H, OCH_2), 6.0–6.4 (m, 2H, CH=CH), 6.79 (d, 1H, ArH, J = 1.72 Hz), 6.81 (d, 1H, ArH, J = 1.72 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.8 (CH_3), 18.4 (CH-CH_3), 55.8 (OCH_2), 64.3 (OCH_3), 108.8 (CH Ar), 112.7 (CH=), 118.7 (C-I), 123.7 (CH), 130.6 (CH), 131.1 (C Ar), 148.2 (C Ar), 149.5 (C Ar).

*2-Methoxy-4-*n*-propylphenol (10)*

Hydrogenation of eugenol (3.0 g, 18.3 mmol) in methanol (75 mL) containing 0.3 g of carbon palladium (10%) was accomplished by treating the mixture under hydrogen pressure (80 bar) for 24 h at 40°C. The mixture, after filtration, afforded compound **10** (2.7 g, 90%) as a green oil. IR (NaCl) (cm^{-1}): 795, 820, 1030, 1120, 1150, 1270, 1430, 1460, 1500, 1600, 2870, 2930, 2960, 3500. ^1H NMR ($CDCl_3$) δ: 0.7 (t, 3H, CH_3), 2.25 (t, 2H, CH_2), 2.85 (t, 2H, CH_2), 3.45 (s, 3H, OCH_3), 5.3 (s, 1H, OH), 6.2–6.7 (m, 3H, ArH).

*2-Bromo-6-methoxy-4-*n*-propylphenol (11)*

A solution of bromine (0.7 mL, 13.6 mmol) in $CHCl_3$ (60 mL) was added dropwise to a solution of **10** (2.0 g, 12.0 mmol) in $CHCl_3$ (100 mL) at 0°C. Once the addition was completed, the mixture was stirred at room temperature for 2 h. The solvent was removed and compound **11** (3.0 g, 100%) was obtained as a beige solid; mp 83°C (lit. (36) value mp +82.5 to 83.5°C). IR (KBr) (cm^{-1}): 820, 860, 960, 1040, 1150, 1200, 1270, 1500, 1590, 2870, 2930, 2950, 3420. ^1H NMR ($CDCl_3$) δ: 0.96 (t, 3H, CH_3), 1.60 (q, 2H, CH_2), 2.60 (t, 2H, CH_2), 3.85 (s, 3H, OCH_3), 6.66 (s, 1H, ArH), 7.08 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$) δ: 13.8 (CH_3), 23.5 (CH_2), 37.9 (CH_2), 56.1 (OCH_3), 112.2 (CH Ar), 114.6 (C-Br), 118.4 (CH Ar), 133.3 (C Ar), 144.3 (C Ar), 145.9 (C Ar).

1-Bromo-2-ethoxymethoxy-3-methoxy-5-propylbenzene (12)

A solution of **11** (2.9 g, 11.8 mmol) in DMF (120 mL) was treated with potassium carbonate (9.0 g, 65.2 mmol) and chloromethylethylether (3.4 mL, 36.6 mmol). After being stirred at 80°C for 18 h, the mixture was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated. The product was purified by chromatography on silica gel (eluent CH_2Cl_2) affording the expected compound **12** (2.5 g, 69%) as a green oil. IR (NaCl) (cm^{-1}): 850, 950, 1160, 1250, 1460, 1500, 2870, 2930, 2960. ^1H NMR ($CDCl_3$) δ: 0.92 (t, 3H, CH_3), 1.15 (t, 3H, CH_3), 1.8 (m, 2H, CH_2), 2.8 (m, 2H, CH_2), 3.78 (q, 2H, OCH_2), 3.85 (s, 3H, OCH_3) 5.24 (s, 2H, OCH_2O), 6.8–7.0 (m, 2H, ArH).

2′-Ethoxy-2-ethoxymethoxy-3,3′-dimethoxy-5′-propenyl-5-propylbiphenyl (13)

Magnesium (0.2 g, 5.0 mmol) and two crystals of iodine in anhyd THF (5 mL) under an N_2 atmosphere were treated with a solution of **9** (1.0 g, 3.1 mmol) in anhyd THF (30 mL). After being stirred at 70°C for 6 h, the mixture was transferred dropwise into a second flask charged with palladium (II) bis-(triphenylphosphine) dichloride (0.2 mg, 0.28 mmol), compound **12** (0.95 g, 3.1 mmol), and 20 mL of anhyd THF. After being stirred at 70°C for 8 h, the mixture was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated. The product was purified by chromatography on silica gel (eluent CH_2Cl_2), affording the expected compound **13** (800 mg, 61%) as an orange oil. ^1H NMR ($CDCl_3$) δ: 0.94 (t, 3H, CH_3), 1.12 (t, 3H, CH_3), 1.35 (m, 3H, CH_3), 1.47 (m, 2H, CH_2), 1.72 (2d, 3H, CH_3-CH=), 3.79 (t, 2H, OCH_2), 3.87 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.15 (s, 2H, OCH_2), 5.22 (s, 2H, OCH_2O), 5.8–6.2 (m, 2H, CH=CH), 6.4–6.8 (m, 4H, ArH).

2′-Ethoxy-2-hydroxy-3,3′-dimethoxy-5′-propenyl-5-propylbiphenyl (III)

A solution of **13** (500 mg, 1.2 mmol) in CH_2Cl_2 (30 mL) was treated with trifluoroacetic acid (0.09 mL, 1.2 mmol). After being stirred at room temperature for 4 h, the mixture was reacted with water. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated to afford the expected compound **III** (*Z* isomer, 200 mg, 46%) as a yellow oil. IR (NaCl) (cm^{-1}): 960, 1050, 1230, 1250, 1500, 2950, 3600. ^1H NMR ($CDCl_3$) δ: 0.92 (t, 3H, CH_3), 1.35 (m, 3H, CH_3), 1.49 (m, 2H, CH_2), 1.75 (2d 3H, CH_3-CH=), 2.64 (m, 2H, CH_2), 3.88 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 4.21 (s, 2H, OCH_2O), 5.8–6.2, m, CH=CH), 6.4–6.8

(m, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 13.8 (CH_3), 14.5 (CH_3), 17.7 (CH_3), 24.2 (CH_2), 37.5 (CH_2), 55.2 (OCH_3), 56.6 (OCH_3), 64.8 (OCH_2), 112.1 (CH), 117.0 (CH), 120.0 (CH), 121.5 (CH), 124.1 (CH), 126.8 (CH), 128.3 (C Ar), 130.5 (C Ar), 130.8 (C Ar), 131.4 (C Ar), 144.3 (C Ar), 145.9 (C Ar), 147.2 (C Ar), 149.1 (C Ar). MS (TMS derivative): 428 ([M]$^+$,100%), 399 (10%), 385 (15%), 73 (32%).

*2-Ethoxy-3,2′-dimethoxy-5-propenyl-4′-propyldiarylether (**IV**)*

A solution of **10** (560 mg, 3.4 mmol) in pyridine (15 mL) was treated with sodium hydride (90 mg, 3.7 mmol) and copper bromide (490 mg, 3.4 mmol). Then compound **9** (550 mg, 1.7 mmol) was added. After being stirred at 125°C for 18 h, the mixture was reacted with a solution of hydrochloric acid (10%). The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated. The products were purified by chromatography on silica gel (eluent CH_2Cl_2) affording **2** (360 mg, 59%) as white crystals; mp 152°C (lit. (33) value mp +152°C), and compound **IV** (20 mg, 3.5%) as a pale oil. IR (NaCl) (cm^{-1}): 790, 1040, 1210, 1260, 1420, 1460, 1500, 1590, 2870, 2930, 2960. ^{1}H NMR ($CDCl_3$) δ: 0.95 (t, 3H, CH_3), 1.27 (t, 3H, CH_3), 1.62, 1.80, 2.56, 3.80, 3.82 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.10 (q, 2H, OCH_2), 6.0 to 6.8 (m, 8H, ArH, and CH=CH). ^{13}C NMR ($CDCl_3$) δ: 13.8 (CH_3), 15.4 (CH_3), 18.2 (CH_3), 24.7 (CH_2), 29.7 (CH_2), 37.8 (OCH_2), 55.8 (OCH_3), 55.9 (OCH_3), 104.3 (CH Ar), 109.0 (CH Ar), 112.9 (CH Ar), 119.2 (CH Ar), 120.6 (CH Ar), 125.1 (CH Ar), 130.5 (CH Ar), 133.3 (C Ar), 138.6 (C Ar), 139.5 (C Ar), 143.7 (C Ar), 148.1 (C Ar), 150.3 (C Ar), 153.9 (C Ar). MS: 356 ([M]$^+$,100%), 327 (20%), 296 (34%), 150 (31%).

Conclusion

Three biphenyl dimers (**I–III**) and one benzylaryl ether (**IV**) were synthesized to show the presence and the importance of phenolic coniferyl alcohol structures in the photoyellowing of high-yield pulps. The dimer **I**, incorporating two propyl chains, was detected in unbleached and sodium borohydride-reduced high-yield pulps in small amounts (≈4 × 10^{-6} mol g^{-1}). It is probably formed by thioacidolysis and Raney nickel treatments from phenolic biphenyl bearing coniferyl aldehyde moieties. Biphenyl **II**, which includes two propenyl chains, was detected in small amounts in peroxide bleached high-yield pulps, in the form of two stereoisomers. Biphenyl **II** probably comes from a ferulic-acid-type structure obtained from an oxidized propenal chain. No arylether **IV** or biphenyl **III** compounds were detected. This result probably indicates that phenolic phenylpropenol units are not present in softwood mechanical pulps, so they do not contribute to the photoyellowing process. A similar conclusion was obtained by us, on the involvement of stilbene phenol leucochromophores (17), and recently confirmed by Johansson et al. (37). After this study and others, the molecular origins of the fast photoyellowing of high-yield pulps remains to be established.

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