Photophysics and photochemistry of a lignin model molecule containing α-carbonyl guaiacyl and 4-hydroxy-3-methoxybenzyl alcohol moieties

Alain Castellan,* Stéphane Grelier, Larbi Kessab, Aziz Nourmamode and Yacine Hannachi

Université Bordeaux 1, Laboratoire de Photophysique et Photochimie Moleculaire, CNRS URA 348, F-33405 Talence Cedex, France

A lignin model molecule (DCOOH), incorporating an α-carbonyl guaiacyl part and a 4-hydroxy-3-methoxybenzyl alcohol moiety linked by an *n*-hexane chain, has been synthesized. The electronic absorption spectra in the ground and excited states (flash photolysis) and the luminescence properties in dilute solutions (alcohol and alkane) and in hydroxypropylcellulose (HPC) film were studied at room temperature and at 77 K in comparison with models representing the two ends. They show that in non-polar and very good hydrogen donor solvents there is interaction between the excited carbonyl and the phenolic group, the chain probably being in a folded conformation. In alcoholic solvents and in HPC films, an intermolecular interaction between the carbonyl chromophore and the hydroxy group of the solvent was observed, the hexamethylene chain being in an extended conformation. UV irradiation of the dimer and the carbonyl monomer, incorporated in an HPC film, show similar reactivity which appears to involve an intermolecular hydrogen abstraction by the excited-state carbonyl group from the surrounding medium. The reactivity of the carbonyl derivatives in isopropyl alcohol and tetrahydrofuran (THF) was found to be similar to that observed for the films. In THF, two isomeric photoadducts between the carbonyl monomer (MCOET) and tetrahydrofuran were isolated and characterized. In alkane solvents, UV irradiation of the dimer leads to the appearance of a new band in the long wavelength range characteristic of the production and oxidation of phenoxyl radicals, which are oxidized to coloured structures such as quinones. The main conclusion of the study is that for the first time, it is shown that in the solid state the carbohydrate matrix does not tend to promote the oxidation process between the carbonyl and the phenol. This result is important for the understanding of the mechanism of photoyellowing of lignin-rich pulps

Introduction

In the last fifty years, intense research has been devoted to the understanding of the mechanisms of the yellowing of bleached lignin-rich pulps when exposed to near UV-light.[1] One reaction pathway of light-induced yellowing is thought[2] to proceed *via* the initial excitation of a conjugated α-carbonyl chromophore and subsequent intersystem crossing to give the triplet state. The triplet excited state species abstracts hydrogen from a neighbouring phenolic hydroxy group of lignin to generate ketyl and phenoxyl radicals; the phenoxyl radical is then oxidized to coloured chromophores such as quinones (Fig. 1).[2,3] The ketyl radical, by reaction with ground-state oxygen, might be oxidized back to the carbonyl entity, to generate a hydroperoxyl radical (Fig. 1).[2,3] Singlet oxygen, formed by energy transfer from the carbonyl excited triplet state, has also been invoked as an activated oxidizing species.[4,5]

Another source of phenoxyl radicals has been found in structures containing β-O-4 aryl ether linkages (Fig. 2).[6-9] The phenoxyl radical is generated by cleavage of the β-O-4 aryl ether bond in ketyl radical structures.[8,9] The latter might be formed either by photoreduction of an α-guaiacylacetoveratrone-type structural element or by abstraction, by a peroxyl radical, of a benzylic hydrogen from a guaiacylglycerol β-arylether group.[9]

The mutual interaction between α-carbonyl and phenolic hydroxy groups, which appears to be very important in lignin photodegradation, has mainly been studied as an intermolecular process involving single chromophore models both in solution[2-4] and in the solid state, adsorbed onto a cellulosic matrix.[10] One must bear in mind that molecular dynamics,

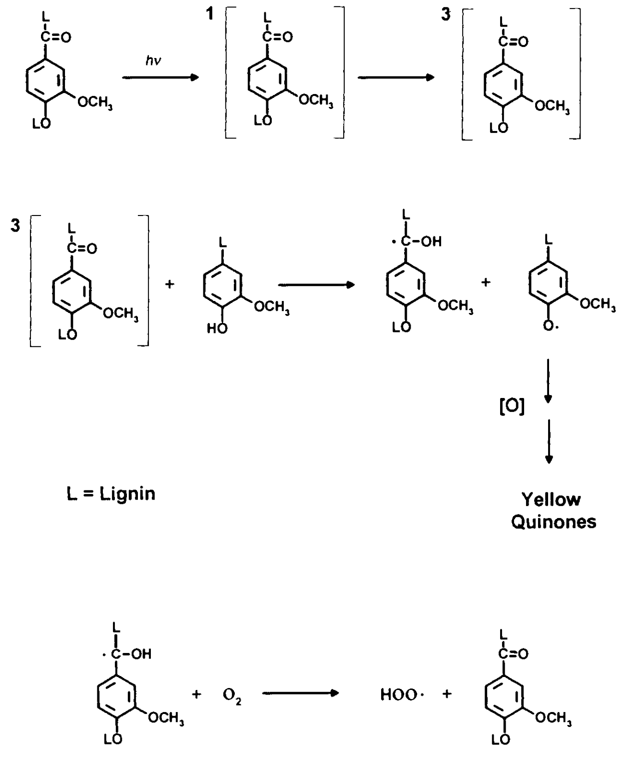


Fig. 1 Mechanism of hydrogen abstraction by α-carbonyl compound in the excited state to form phenoxyl radical according to refs. 2 and 3

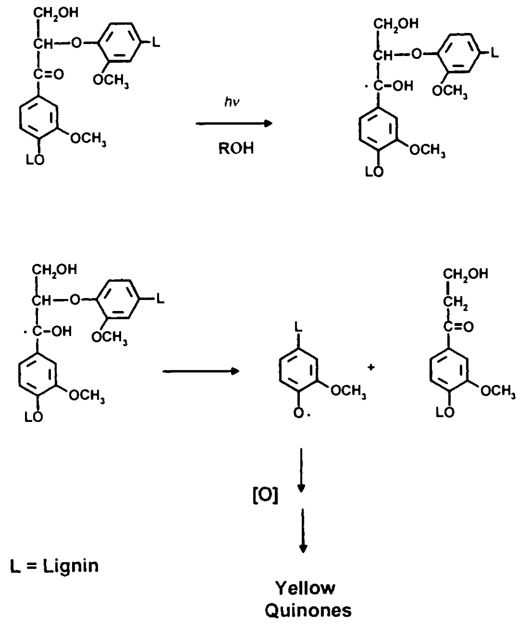
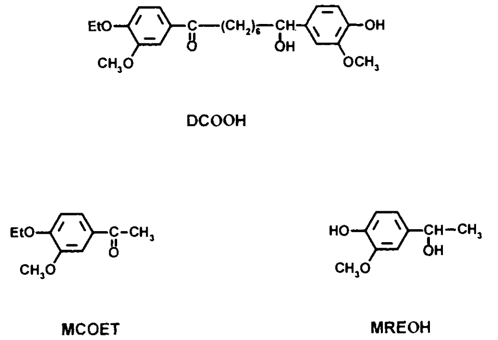


Fig. 2 Mechanism of formation of phenoxyl radical from a β-O-4 structure according to refs. 6–9


DCOOH

MCOET

MREOH

Fig. 3 Formulae of the compounds studied

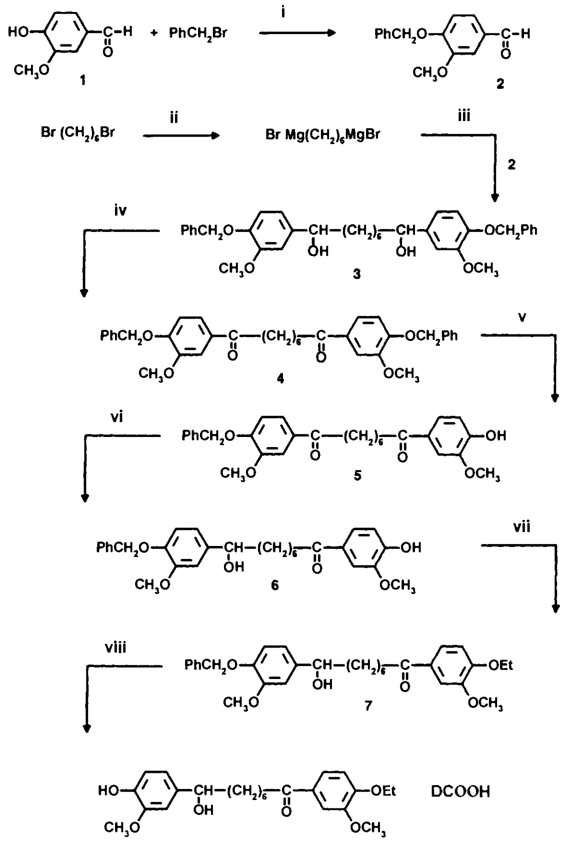


Fig. 4 Synthetic approach to compound DCOOH. *Reagents and yields*: i, K_2CO_3, acetone, 94%; ii, Mg, Et_2O, room temperature (RT); iii, Et_2O, reflux, 64%; iv, MnO_2, acetone, RT, 90%; v, H_2, Pd–C, THF, RT, 33%; vi, $NaBH_4$–NaOH, EtOH, RT, 75%; vii, EtI, K_2CO_3, acetone, reflux, 90%; viii, Pd–C, HCO_2NH_4, acetone, reflux, 95%.

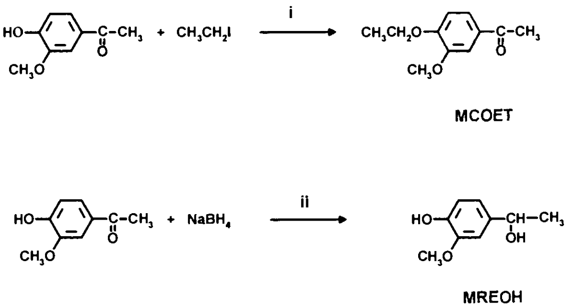


Fig. 5 Synthetic approach to compound MCOET and MREOH. *Reagents and yields*: i, EtI, K_2CO_3, acetone, reflux, 80%; ii, $NaBH_4$, EtOH, RT, 74%.

which exist in the solid phase, are more likely to be important than for a solution phase system which allows easy molecular diffusion of intermediates such as free radical species or yellow photoproducts in order that they may react. In the pulp environment itself, chromophoric groups are held fairly rigidly by the three-dimensional polymer matrix thus making material diffusion almost impossible. In this respect, the results presented in this article concern a photophysical and photochemical study of a 2-hydroxypropylcellulose solid matrix (HPC) supporting a lignin model molecule DCOOH containing an α-carbonyl guaiacyl part and a 4-hydroxy-3-methoxybenzyl alcohol moiety linked by an *n*-hexane chain. The lignin model dimer with the hexane linkage between the two moieties mimics the restrained environment of the lignin matrix and HPC simulates the cellulosic polymer matrix. For comparison, similar experiments were performed in fluid solution and on the monomer molecules MCOET and MREOH (Fig. 3).

Results and discussion

Synthesis

The route chosen for the synthesis of the bichromophore DCOOH and the reference monomers MCOET and MREOH is outlined in Figs. 4 and 5. The phenolic group of vanillin **1** was protected as a benzyl ether. Reaction of hexane-1,6-diyldimagnesium bromide with the protected aldehyde **2** and oxidation, by manganese dioxide, of the dibenzylic alcohol **3**, allowed the preparation of the protected di-α-carbonyl bichromophore **4** with a total yield, starting from vanillin **1**, of 54%. By careful control of hydrogenolysis experimental conditions, it was possible to deprotect only one phenolic function of compound **4** and prepare the dissymmetrical bichromophore **5** in reasonable yield (33%). The synthesis of compound **6** (yield 75%) takes advantage of the selective reduction with sodium borohydride, in basic media (pH ~ 14), of the carbonyl group in the *para* position of the etherified phenol. The reaction was much more rapid than the reduction of the carbonyl function situated in the *para* position of the phenol. This situation has already been observed on other lignin model molecules.[11] Compound **6** was etherified (yield 90%) with ethyl iodide and potassium carbonate according to usual procedure. The final deprotection of the remaining phenolic group was found to be successful (yield 95%), by using a procedure employed in the glycosidic series;[12] the catalyst used was still palladium on activated carbon but the hydrogen source was ammonium formate instead of hydrogen gas. The reference monomer derivatives, MCOET and MREOH were prepared

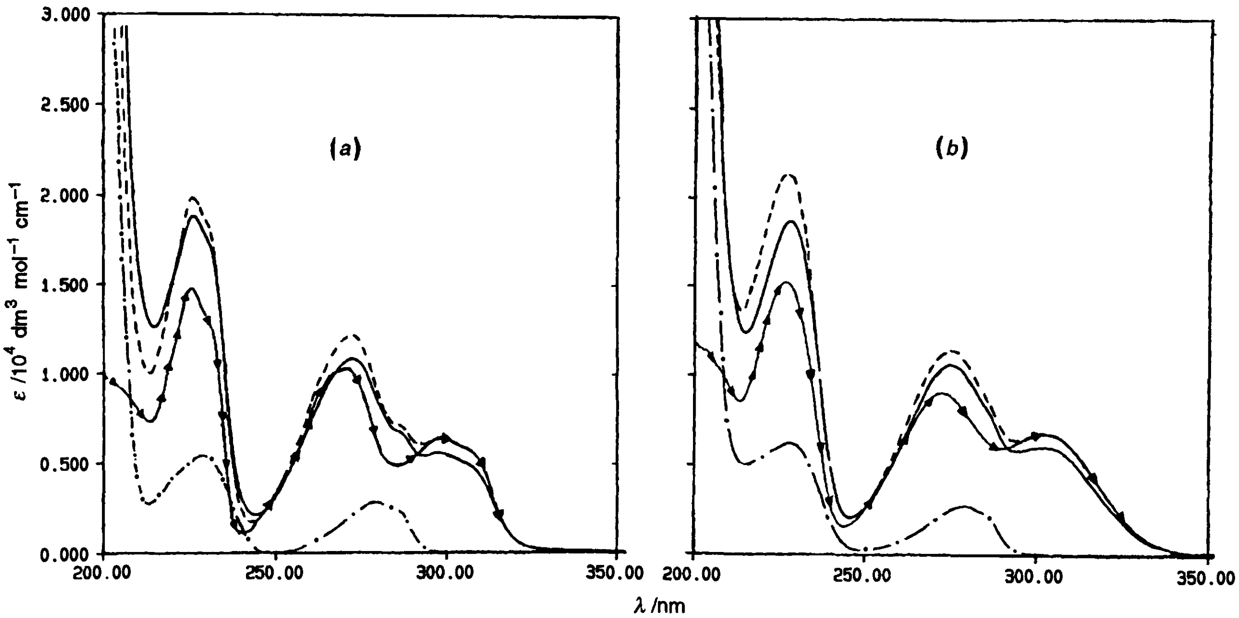


Fig. 6 UV absorption spectra at room temperature in MeOBu^t (*a*) and in methanol (*b*) of DCOOH (——) (concentration ≈ 10^{-4} mol dm^{-3}) compared with models of the different moieties: MREOH (—•—), MCOET (—▸—), MREOH (ε) + MCOET (ε) (— — —)

using standard procedures for etherification of phenols and reduction of carbonyl groups. The bichromophore and the reference compounds were purified by column chromatography (silica gel) and the purity was checked by HPLC (C18 reversed-phase). The molecular structure of the bichromophore was established by ^{1}H and ^{13}C NMR, mass spectrometry (low and high resolution), IR and UV absorption spectrometry. The ^{1}H, ^{13}C NMR chemical shifts are given in the Experimental section. The assignments were made by reference to the work of Mörck and Kringstad on lignin model compounds,[13] and are in agreement with the DEPT and HMQC (^{1}H-detected multiple quantum coherence) spectra.

Electronic absorption spectra

UV absorption spectra are sensitive to molecular interactions in the ground state and the technique has been applied to linked systems.[14] The absorption spectra of the bichromophore DCOOH (concentration ≈ 10^{-4} mol dm^{-3}) in *tert*-butyl methyl ether (non-polar solvent) and methanol (protic polar solvent), presented in Fig. 6, and compared with the sum of the absorption of the reference monomer compounds (MCOET and MREOH), do not reveal strong intramolecular interactions in the ground state between the aromatic moieties. As for other methoxylated alkylphenones,[15] the ketones MCOET and DCOOH in MeOBu^t show the normal electronic π–π* charge transfer bands of the substituted benzene chromophore. The n–π* band, observed in non-polar solvents, as a small shoulder on the long wavelength side of the π–π* band [Fig. 6(*a*)] is completely hidden beneath the π–π* band in polar solvents such as methanol [Fig. 6(*b*)]. This solvent effect is general for phenyl alkyl ketones[15] and has also been observed in acetonitrile for the carbonyl monomer and dimer compounds.

Luminescence spectra

The reference compound MCOET and the bichromophore DCOOH display luminescence (Fig. 7) at 77 K in rigid matrices (methylcyclohexane, ethanol glasses and hydroxypropylcellulose (HPC) films, concentration ≈ 10^{-4} dm^3 mol^{-1}, λ_{exc} = 310 nm). This is in contrast with room temperature experiments where no emission was observed for the solution. The only detected emission was for the HPC film (Fig. 7), the latter being fluorescence from the carbohydrate polymer[16] and not from the carbonyl derivatives.

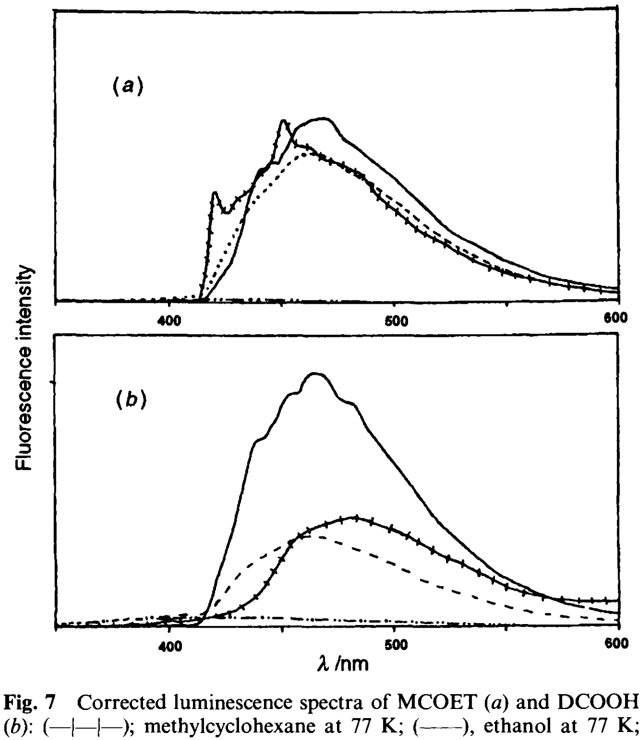


Fig. 7 Corrected luminescence spectra of MCOET (*a*) and DCOOH (*b*): (—|—|—); methylcyclohexane at 77 K; (——), ethanol at 77 K; (— — —), HPC at 77 K; (— · · —), HPC at 300 K (λ_{exc} = 310 nm, concentration ≈ 10^{-4} mol dm^{-3})

The luminescence spectra recorded at 77 K correspond to phosphorescence emission; similar spectra (not shown) were obtained with the spectrometer equipped with a phosphorescence accessory. The same phosphorescence lifetimes were measured for the dimer and the monomer in MCH (320 ms) and ethanol (480 ms). Slightly different values were obtained for the HPC films (DCOOH: 500 ms; MCOET: 370 ms). These observations correllate well with those found on other α-carbonyl lignin model derivatives[7b,17] and are indicative of a low-lying π–π* excited triplet state.

The phosphorescence spectra of the monomer and the dimer in ethanol glass are very similar and are characteristic of a carbonyl chromophore interacting with hydroxy groups of the solvent. In non-polar solvents, such as methylcyclohexane, the

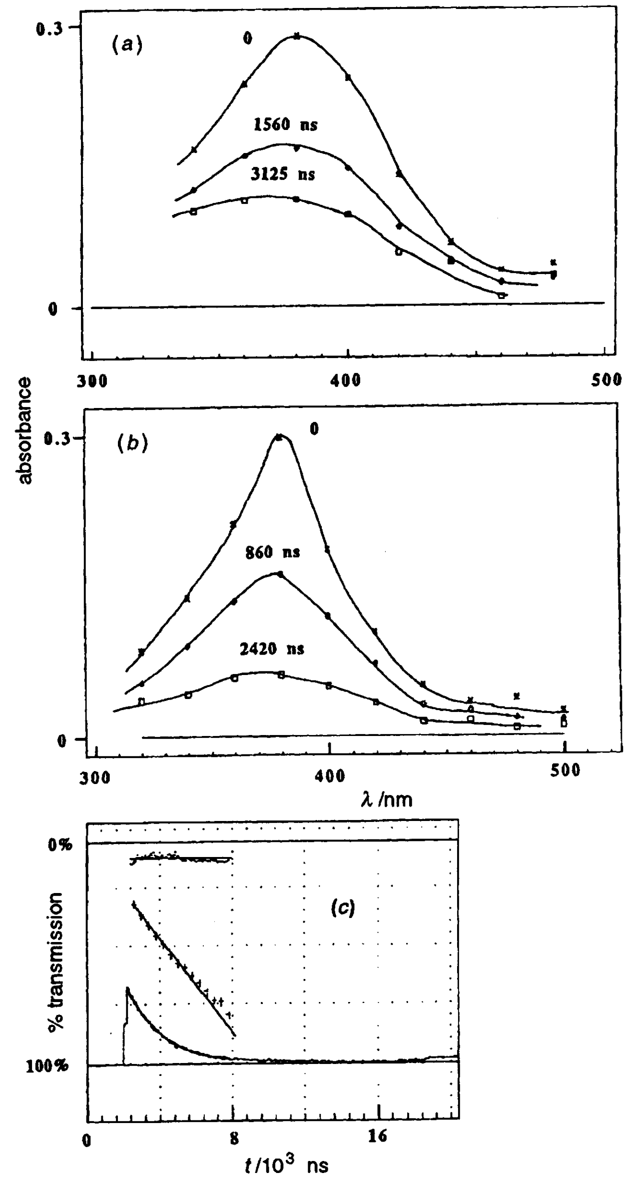


Fig. 8 (*a*) Transient absorption spectra of the carbonyl compounds in nitrogen-degassed tetrahydrofuran (concentration $\approx 10^{-4}$ mol dm^{-3}, λ_{exc} = 266 nm) measured just after the excitation and after some delays: (*a*) DCOOH; (*b*) MCOET; (*c*) trace of the decay measured at 380 nm for MCOET

dimer phosphorescence spectrum reveals strong intramolecular interactions between the two moieties, probably between the phenolic group and the carbonyl chromophore. In this solvent, arrangements with a folded conformation of the methylene chain, which allow strong interactions between the carbonyl and the phenol group, are certainly the most favourable. The shape of the spectra recorded at 77 K from the HPC films, similar for both compounds, indicates strong interactions between the excited carbonyl chromophore and the hydroxy groups probably from the HPC polymer. Dimer conformations with extented methylene chain arrangements preventing intramolecular interactions of the end groups, are probably the most stable conformations in the films.

Flash photolysis

UV excitation of compounds MCOET and DCOOH by a laser flash (Nd-YAG, λ_{exc} = 266 nm, duration 200 ps) produced transient absorptions. The spectra recorded at different delays from the excitation of detection are reported in Fig. 8. The transient with λ_{max} = 390 nm is readily ascribable to an absorption from the lowest triplet state, on the basis of its similarity to the published spectra for substituted acetophenones and a previous report on the transient absorption of α-carbonyl lignin model molecules.^{7a,9a,18} The triplet decay (at 380 nm; insert, Fig. 8) was monitored for two solvents: isopropyl alcohol and THF in the absence and presence of oxygen (two concentrations). The triplet lifetimes in degassed media were measured for DCOOH (3350 ns in isopropyl alcohol and 1150 ns in THF) and for MCOET (9300 ns for isopropyl alcohol and 1900 ns for THF). The quenching rate constants k_q of the triplet

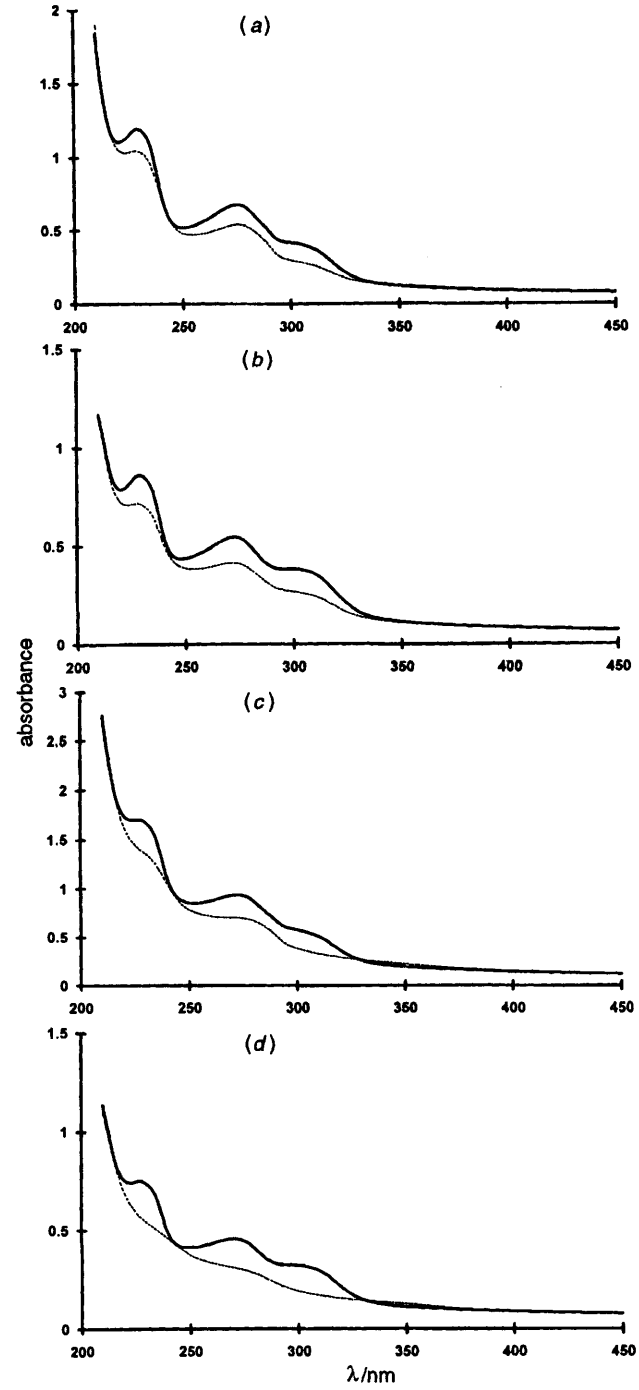


Fig. 9 (*a*) Absorption spectra of DCOOH in HPC film prepared from a methanol solution and irradiated at 320 nm: (——), before irradiation; (— — —), 4 h irradiation; (*b*) absorption spectra of MCOET in HPC film prepared from a methanol solution and irradiated at 320 nm: (——), before irradiation; (— — —): 4 h irradiation; (*c*) absorption spectra of DCOOH in HPC film prepared from a tetrahydrofuran solution and irradiated at 320 nm: (——), before irradiation; (— — —), 1 h irradiation; (*d*) absorption spectra of MCOET in HPC film prepared with a THF solution and irradiated at 320 nm: (——), before irradiation; (— — —), 1 h irradiation state by oxygen for both compounds were found to be very similar for the two solvents: (4 ± 1) × 10^9 dm^3 mol^{-1} s^{-1}. k_q was calculated from the slope of the plot of $1/\tau$ *vs.* ([O_2]) which was found to be linear. The values are typical for triplet quenching by oxygen and leave no doubt as to the identity of the observed transient. For both compounds, a shortening of the triplet lifetime was observed in tetrahydrofuran compared with isopropyl alcohol. Both solvents are very good hydrogen donors, but isopropyl alcohol is much more polar than THF and the expected trend is an increase in the energy of the n–π^* triplet state and a decrease in the energy of the π–π^* triplet state on going from non-polar to polar solvents.[18] The chemical decay channel due to the formation of ketyl radicals usually occurring from the n–π^* component of the triplet state appears to be favoured by THF rather than isopropyl alcohol. This is confirmed by the photochemical studies. Some residual absorption at 390 nm remains after a few microseconds delay from the laser flash excitation. This is probably due to ketyl radicals formed by photoreduction of the carbonyl group and also to some phenoxyl radical produced by demethylation of the aromatic ring (see the photochemistry of the HPC films made from THF solutions). The shorter triplet lifetime observed for the bichromophore compared with the monomer in both solvents is probably ascribable to some intramolecular interactions between the carbonyl triplet and the phenolic group, nevertheless this interaction was not observed in the photochemistry experiments involving THF solutions.

Photochemistry

The main purpose of this study was to obtain information on the role of the matrix on the photoyellowing of phenolic groups sensitized by conjugated α-carbonyl chromophores. Is the matrix capable of transferring the peroxidic radicals generated near the carbonyl to oxidize the very sensitive 4-hydroxy-3-methoxybenzyl alcohol structure at a distance fixed by the motions of the hexane chain? For this purpose, the bichromophore incorporated in the HPC matrix was irradiated with monochromatic light at 320 nm at which only the carbonyl chromophore absorbs the radiation. Luminescence studies suggested extended conformations of the hexamethylene chain in protic solvents and folded conformations in non-polar solvents, the driving force being the interactions between the carbonyl and the hydroxy groups.

The HPC films were prepared by evaporation in a quartz cuvette of a solution (methanol or tetrahydrofuran) of the chromophore and the carbohydrate polymer. The experimental conditions were chosen to favour intramolecular interactions between the two moieties of the lignin dimer molecule (see the Experimental section). The absorption spectra of the films containing DCOOH and MCOET before and after UV irradiation are reported in Fig. 9(*a*), (*b*) (films obtained from methanol solutions) and (*c*), (*d*) (films obtained from THF solutions). The film obtained from methanol solution and containing MREOH, a monomer without carbonyl groups, does not reveal any photoreactivity compared with the carbonyl derivatives. In contrast, the latter compounds incorporated into films prepared from methanol solutions [Fig. 9(*a*), (*b*)] show consumption of the conjugated carbonyl structures with no concomitant increase of absorption bands in the long-wavelength side. When the HPC films were prepared from THF solutions, very rapid consumption of the carbonyl chromophores is seen together with the appearance of a band at longer wavelengths. The same effect was observed when polystyrene or poly(methyl methacrylate) were used instead of HPC. This observation is remininiscent of the photoyellowing of milled-wood lignin incorporated into HPC films.[19]

The photoreactivity of the monomers (MREOH and MCOET) and the dimer DCOOH was also studied in fluid solution to correlate the behaviour of the molecules with the

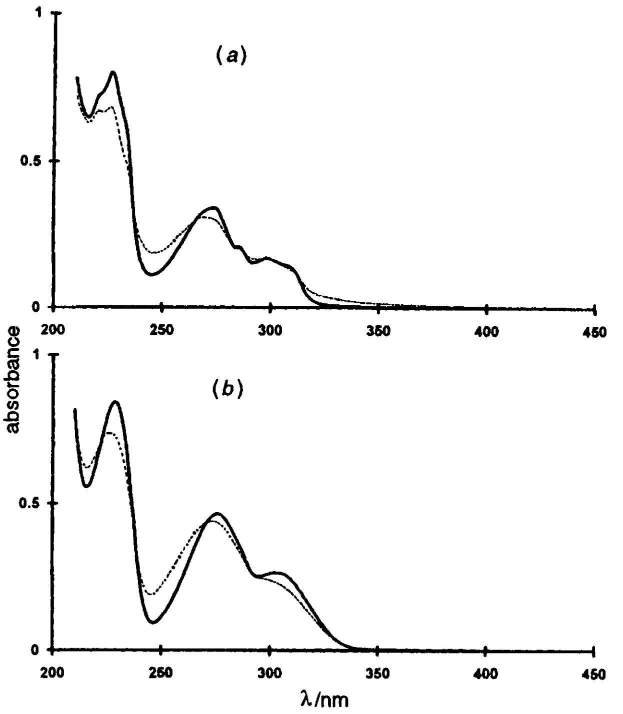


Fig. 10 (*a*) Absorption spectra of DCOOH in hexadecane irradiated at 320 nm: (——), before irradiation; (— — —), 3 h irradiation; (*b*) absorption spectra of DCOOH in isopropyl alcohol irradiated at 320 nm: (——), before irradiation; (— — —), 3 h irradiation

different conformations observed by phosphorescence spectroscopy. Hexadecane was chosen to mimic a viscous hydrophobic medium, isopropyl alcohol was selected as a good hydrogen donor alcohol and tetrahydrofuran because the HPC films are easily made with this solvent. The two monomers were found to be photostable in hexadecane solutions. In contrast, with the dimer, a band is formed at longer wavelengths which contributes to the photoyellowing when the solutions are more concentrated [Fig. 10(*a*)]. The formation of this band might be interpreted by the mechanism given in Fig. 1 with an intramolecular interaction between the carbonyl group and the phenol function.

The monomers were also found to be photostable in isopropyl alcohol. In this solvent, the dimer displays a minor consumption of the carbonyl group [Fig. 10(*b*)] without formation of any new bands at longer wavelengths. In THF, the same effect is also observed for the carbonyl derivatives MCOET and DCOOH, but with a significant increase in the conversion rates [Fig. 11(*a*), (*b*)]. It was noted that when 20% (by volume) of THF was added to the MCOET hexadecane solution, some consumption of the carbonyl monomer was observed. As with many ethers, tetrahydrofuran has good hydrogen donating ability, this explains its easy autooxidation. This property is in accordance with the rapid consumption of the carbonyl chromophores in THF solution and in the HPC films prepared from THF solutions. Moreover, results of flash photolysis studies are in accordance with the increase in the photoreactivity of the carbonyl derivatives in THF, the contribution of the n–π^* component of the triplet being more important in this solvent than in isopropyl alcohol.[18] The formation of the long wavelength band in the films prepared from THF might be due to a demethylation process as observed by Weir *et al.* for poly(acrylphenones).[20]

The monomer MCOET was irradiated in THF solution with a high conversion rate of the carbonyl chromophore and the mixture was separated by reversed-phase HPLC (C18 silica gel; eluent: methanol). The chromatogram is shown in Fig. 12. The starting material and the reduced carbonyl derivative were characterized by comparison with authentic samples and by

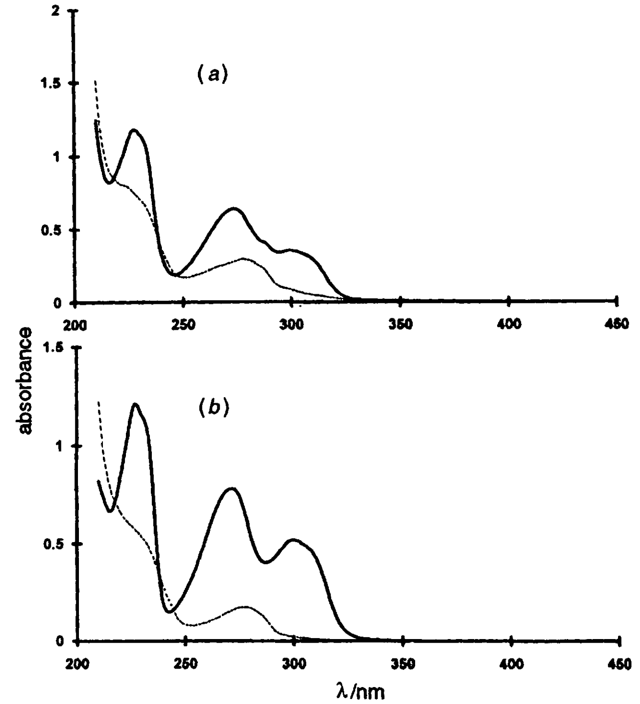


Fig. 11 (*a*) Absorption spectra of DCOOH in THF irradiated at 320 nm: (——), before irradiation; (— — —), 2 h irradiation; (*b*) absorption spectra of MCOET in THF irradiated at 320 nm: (——), before irradiation; (— — —), 2 h irradiation

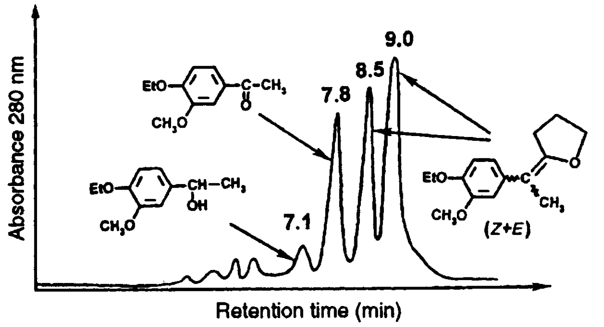


Fig. 12 HPLC chromatogram of the irradiation mixture of MCOET irradiated in THF solution at 320 nm (C18 reversed-phase column, eluent methanol)

their mass spectra (LSIMS ionization). The peaks at 8.5 and 9.0 min retention times were attributed to the two isomers depicted in Fig. 13, in accordance with their mass spectrum (LSIMS ionization), which are identical and present a peak at 249 mu $(M + H)^+$. The UV spectrum obtained after irradiation of the MCOET tetrahydrofuran solution was typical of the photoreduction of the carbonyl chromophore, nevertheless, after HPLC separation of the irradiating mixture, the compounds corresponding to the peaks at 8.5 and 9 min showed a significant absorption at wavelengths above 300 nm, characteristic of styrenic derivatives. These compounds are probably formed by dehydration, on the chromatographic support of the column, of the benzylic alcohol formed by coupling of the tetrahydrofuryl and ketyl radicals (Fig. 13).

For the MCOET and DCOOH compounds incorporated into HPC films obtained from THF solutions, photoreduction and coupling between the ketyl and the tetrahydrofuryl radicals probably occur. At the same time, the demethoxylation process probably contributes to the formation of the band absorbing at long wavelength. In the HPC films obtained from methanol solutions, the photoreduction of the carbonyl group appears to be the only photochemical process occurring.

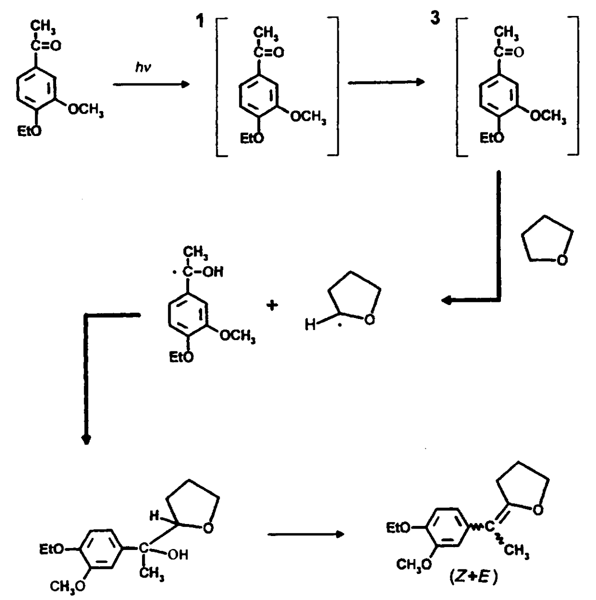


Fig. 13 Mechanism of formation of the photoproduct isolated from the irradiation of MCOET in THF solution

Conclusions

This work demonstrates that the use of a lignin model dimer such as DCOOH is very useful to study the dependence on the medium of the oxidation of *p*-hydroxybenzyl alcohol into phenoxyl radical sensitized by a conjugated α-carbonyl chromophore, this problem having been discussed for many years in relation to the photoyellowing of lignin-rich pulps. In fluid solution, where molecular motions are very easy, when the solvent is non-polar and not a good hydrogen donor, intramolecular hydrogen abstraction of the phenol by the triplet carbonyl occurs and a long wavelength absorption band is formed. When the solvent is a good hydrogen donor (isopropyl alcohol and tetrahydrofuran), intermolecular hydrogen abstraction from the solvent by the carbonyl is the main process, the reactivity being more significant with the low polarity solvent. This is due to an increase in the participation of the n–π* configuration in the lowest triplet state which has mainly π–π* character. The observed reactivity is in accordance with luminescence studies which indicates that extended conformations of the link are most favourable in polar solvents and folded conformations of the link are the most favourable in an alkane solvent, the driving force being the interactions between the carbonyl chromophore and the phenolic group. Irradiation of the dimer in comparison with the reference monomer incorporated into hydroxypropyl films shows a rapid intermolecular hydrogen abstraction by the carbonyl from the surrounding medium, with no observed intramolecular interactions between the phenol and the carbonyl groups. Long wavelength absorption bands were noted for the carbonyl monomer and dimer molecules, which probably indicate the cleavage of the ether bond of the methoxy substituent of the benzenic ring of the acetophenone moiety. Propagation of the oxidation of the phenol by the carbonyl in a solid carbohydrate matrix does not appear to be a major process, photoreduction of the carbonyl by a hydroxy group of the matrix being more favoured in this polar environment. Nevertheless, if the lignin polymer is hydrophobic enough to encounter interactions between the phenol and the carbonyl group, such a process might operate as shown by the bichromophore in an alkane solvent. So, among the mechanisms that account for the reactivity of α-carbonyl structural elements of lignin during the photoyellowing of high-yield pulps, β-*O*-4 benzyl-aryl ether cleavage, previously studied,[7–9] appears the most important.

Experimental

General and physical methods

Mps were taken with a heating microscope (Reichter) and are uncorrected. A microbalance (Mettler ME 30, sensitivity 1 µg) was used to weigh the samples for spectrometric measurements. NMR spectra were recorded on Hitachi R1200 (60 MHz) and Bruker AC 250 (FT 250 MHz) spectrometers (reference Me_4Si, solvent $CDCl_3$). IR and electronic absorption spectra were run on Perkin-Elmer 412 and Hitachi U3300 instruments. Mass spectra were obtained using a VG autospec Q spectrometer. The spectra were obtained with the usual electron bombardment ionization (70 eV) mode or with the LSIMS ionization mode. The fluorescence spectra were recorded with a Hitachi F4500 fluorimeter. The fluorescence spectra were automatically corrected in the emission mode by the software of the apparatus. The purity of the compounds was checked by TLC (silica gel) and HPLC (Lichrosorb NH_2, 5 µm, length 25 cm, eluent CH_2Cl_2 or Nucleosil C_{18} reversed-phase, 5 µm, length 25 cm, eluent methanol).

For the preparation of the films, the compounds (0.2–0.5 mg) were dissolved in 2.5 cm^3 of tetrahydrofuran (THF, spectrophotometric grade) or methanol (twice distilled) and 0.25 cm^3 of water. 2-Hydroxypropylcellulose (Hercules, Klucel E 60, 200 mg) was then added and the mixture was shaken until the HPC dissolved completely. The solution was then placed in an open quartz cell (1 mm deep) and evaporated in a circulating air oven (35 °C) to dryness leaving a transparent film, suitable for absorption measurements. The concentration of the dimer in the HPC matrix was estimated to be 5×10^{-4} mol dm^{-3}. These experimental conditions favour intramolecular interactions between the two moieties. The films were irradiated with monochromatic light ($\lambda = 320$ nm) delivered by a Xenon lamp (2 kW) equipped with a Jobin-Yvon monochromator. For the solution irradiations, 1 cm and 1 mm cells were used.

The transient absorption measurements were made by laser flash photolysis using the 266 nm wavelength of a Q-switched neodymium-YAG laser (Quantel Instruments). The analysis beam from a pulsed 75 W xenon lamp was perpendicular to the laser beam and passed through an electrical shutter (to avoid the formation of stable photoproducts) and then to a quartz cell containing the sample. The apparatus and the technique have been described in more detail elsewhere.[21]

All compounds synthesized were purified by careful column chromatography on silica gel with appropriate eluents. Commercial starting materials were obtained from Aldrich, and solvents (chromatographic and/or spectrometric quality), from SDS (*Solvants-Documentation-Synthèses*, Marseille) and Aldrich. No fluorescent impurities in the solvents were detected under our experimental conditions before luminescence measurements.

Syntheses

4-Benzyloxy-3-methoxybenzaldehyde (2). To a stirred solution of vanillin (10 g, 66 mmol) in dry acetone (150 cm^3) was added, under nitrogen, dry potassium carbonate (10 g, 72 mmol) and benzyl bromide (12 g, 70 mmol), after which the mixture was refluxed for 6 h with magnetic stirring. After being cooled to room temperature, the reaction mixture was filtered and hydrolysed with water (500 cm^3). The mixture was then extracted with methylene chloride (300 cm^3) and the organic phase was dried with sodium sulfate and evaporated under reduced pressure. Addition of light petroleum allowed the isolation of pale yellow crystals of compound **2** (94%), mp 58 °C, $\delta(CDCl_3$; 60 MHz) 3.76 (3 H, s), 5.03 (2 H, s), 6.6–7.4 (8 H, m) and 9.53 (1 H, s); ν_{max}(KBr)/cm^{-1} 3040, 3020, 2990, 2820, 2720, 1680, 1580, 1450, 1420, 1390, 1340, 1250, 1190, 1150, 1130, 1080, 1020, 990, 900, 850, 800, 770, 720 and 690; *m*/*z* 242 (5%, $M^{+\bullet}$), 91 (100) and 28 (25).

1,8-Bis(4-benzyloxy-3-methoxyphenyl)octane-1,8-diol (3). To the Grignard reagent prepared from 1,6-dibromohexane (6 g, 25 mmol) and magnesium (1.2 g, 50 mmol) in dry ethyl ether (250 cm^3), compound **2** (12 g, 50 mmol) dissolved in dry benzene (80 cm^3) was added dropwise. The mixture was refluxed for 2 h, cooled and washed successively with dilute hydrochloric acid and water. The organic phase was dried over sodium sulfate and evaporated under reduced pressure. The crude oil after treatment with boiling diethyl ether afforded white crystals of compound **3** (64%), mp 97 °C, $\delta(CDCl_3$; 60 MHz) 1–1.9 (12 H, m), 2.1 (2 H, s), 3.90 (6 H, s), 4.6 (2 H, t), 5.15 (4 H, s) and 6.8–7.8 (16 H, m); ν_{max}(KBr)/cm^{-1} 3400, 3060, 3030, 3000, 2920, 2860, 1600, 1520, 1480, 1450, 1390, 1260, 1230, 1140, 1060, 1040, 1010, 980, 900, 870, 850, 800, 730, 690 and 640; *m*/*z* 593 [7%, $(M + Na)^+$], 570 (52, $M^{+\bullet}$), 553 (94), 535 (24), 463 (50), 445 (43) and 321 (37).

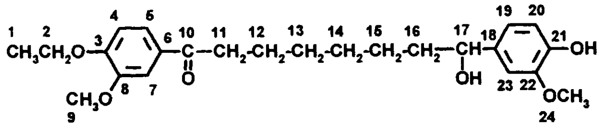
1,8-Bis(4-benzyloxy-3-methoxyphenyl)octane-1,8-dione (4). A mixture of **3** (10 g, 17.5 mmol) and manganese dioxide (8 g, 92 mmol), prepared from manganese sulfate and potassium permanganate according to Fatiadi,[22] were added to dry acetone (400 cm^3) and stirred under nitrogen atmosphere for 4 h at room temperature. After filtration, the solution was evaporated to dryness under vacuum. The residue after chromatography on silica gel (eluent methylene chloride) afforded compound **4** as a white solid (90%), mp 136 °C, $\delta(CDCl_3$, 60 MHz) 1–2 (8 H, m), 2.5 (4 H, t), 3.90 (6 H, s), 5.06 (4 H, s) and 6.3–7.6 (16 H, m); ν_{max}(KBr)/cm^{-1} 3060, 3020, 2980, 2920, 2830, 1680, 1580, 1500, 1470, 1450, 1410, 1380, 1320, 1260, 1230, 1140, 1020, 1000, 980, 970, 870, 850, 770, 730, 690 and 640; *m*/*z* 566 (8%, $M^{+\bullet}$), 548 (2), 475 (4), 304 (12), 214 (10) and 91 (100).

1-(4-Hydroxy-3-methoxyphenyl)-8-(4-benzyloxy-3-methoxyphenyl)octane-1,8-dione (5). Compound **4** (1 g, 1.77 mmol) and Pd–C (5%, 80 mg) in THF (100 cm^3) were stirred vigorously in the presence of hydrogen gas at atmospheric pressure for 7 min. The mixture was filtered and the solvent evaporated off under reduced pressure. The residual oil was purified by chromatography on silica gel (eluent methylene chloride) to yield compound **5** as a white solid (33%), mp 84 °C, $\delta(CDCl_3$; 60 MHz) 1–1.8 (8 H, m), 2.8 (4 H, t), 3.79 (3 H, s), 3.81 (3 H, s), 5.11 (2 H, s), 6.3 (1 H, s) and 6.6–7.6 (11 H, m); ν_{max}(KBr)/cm^{-1} 3500, 3060, 3020, 2990, 2920, 2840, 1660, 1600, 1580, 1500, 1470, 1450, 1410, 1380, 1320, 1260, 1210, 1140, 1020, 1000, 980, 970, 900, 860, 840, 800, 830, 800, 730, 690 and 640; *m*/*z* 476 (7%, $M^{+\bullet}$), 368 (5), 271 (12), 151 (25), 91 (100), 57 (42) and 28 (36).

1-(4-Hydroxy-3-methoxyphenyl)-8-(4-benzyloxy-3-methoxyphenyl)-8-hydroxyoctan-1-one (6). To a solution of compound **5** (0.2 g, 0.42 mmol) in ethanol (50 cm^3) was added sodium hydroxide (0.4 M; 5 cm^3) and sodium borohydride (100 mg, 2.6 mmol). The mixture was stirred for 30 min at room temperature and then acidified with dilute hydrochloric acid. Extraction with methylene chloride and usual work-up of the organic phase afforded, after purification by chromatography on silica gel (methylene chloride–ethyl ether 9:1 v/v) compound **6** as a white solid (91%), mp 88 °C, $\delta(CDCl_3$; 60 MHz) 1–2 (11 H, m), 2.8 (2 H, t), 3.78 (3 H, s), 3.83 (3 H, s), 4.51 (1 H, t), 5.04 (2 H, s), 6.2 (1 H, s) and 6.6–7.6 (11 H, m); ν_{max}(KBr)/cm^{-1} 3500, 3060, 3020, 2920, 2850, 1670, 1590, 1520, 1460, 1420, 1380, 1260, 1140, 1030, 980, 900, 780, 630 and 640; *m*/*z* 501 [6%, $(M + Na)^+$], 478 (17), 461 (100), 371 (16), 243 (10) and 227 (15).

1-(4-Ethoxy-3-methoxyphenyl)-8-(4-benzyloxy-3-methoxyphenyl)-8-hydroxyoctan-1-one (7). To compound **6** (150 mg, 0.32 mmol) in dry acetone (50 cm^3) was added under nitrogen gas, dry potassium carbonate (100 mg, 0.75 mmol) and ethyl iodide (200 mg, 1.2 mmol), and the mixture was refluxed for 2 h. After being cooled to room temperature, the reaction mixture was extracted with methylene chloride and the organic phase worked up as usual. After chromatography of the crude product on silica gel (eluent methylene chloride) compound 7 was isolated as an oil (90%), δ($CDCl_3$; 60 MHz) 1–2 (14 H, m), 2.8 (2 H, t), 3.78 (3 H, s), 3.83 (3 H, s), 4.05 (2 H, q), 4.49 (1 H, t), 5.04 (2 H, s) and 6.6–7.6 (11 H, m); ν_{max}(NaCl)/cm^{-1} 3480, 3080, 3040, 3020, 2990, 2950, 2890, 1685, 1600, 1530, 1470, 1440, 1400, 1340, 1270, 1160, 920, 895, 880, 850, 800, 750, 700, 650 and 730; *m/z* 506 (20%, $M^{+\cdot}$), 489 (100), 399 (15), 293 (6), 264 (14) and 241 (11).

1-(4-Ethoxy-3-methoxyphenyl)-8-(4-hydroxy-3-methoxyphenyl)-8-hydroxyoctan-1-one DCOOH. A mixture of 7 (100 mg, 0.2 mmol) ammonium formate (100 mg, 1.6 mmol) and Pd–C (5%, 100 mg) in dry acetone was refluxed for 1 h. After filtration, the solution was evaporated under reduced pressure and the residue chromatographed on silica gel [eluent methylene chloride–ethyl ether (9:1 v/v)] to yield compound DCOOH as an oil (95%), δ_H($CDCl_3$: 250 MHz) 1–1.8 (14 H, m), 2.8 (2 H, t), 3.77 (3 H, s), 3.83 (3 H, s), 4.06 (2 H, q), 4.46 (1 H, t) and 6.6–7.6 (7 H, m); δ_C($CDCl_3$; 62.8 MHz) 14.6 (C1), 24.7, 25.8, 29.3, 29.4 (C12, C13, C14, C15), 38.0 (C11), 39.0 (C16), 55.8 (C9, C24), 64.4 (C2), 74.5 (C17), 108.5, (C7), 110.3 (C23), 110.9 (C4), 114.2 (C19), 118.9 (C20), 122.8 (C5), 129.9 (C6), 137.0 (C18), 145.0 (C21), 146.7 (C8), 149.1 (C22), 152.6 (C3) and 199.5 (C10); ν_{max}(KBr)/cm^{-1} 3500–3100, 3060, 2920, 2840, 1670, 1580, 1510, 1460, 1405, 1395, 1370, 1260, 1150, 1090, 1040, 970, 890, 850, 800, 760, 710 and 645; *m/z* 455 [27%, $(M + K)^+$], 416 (6%, $M^{+\cdot}$), 399 (100), 355 (8), 264 (10) and 209 (10); high resolution MS calculated on a compound giving only one peak on HPLC [reversed-phase C18 (eluent methanol) or silica (eluent dichloromethane)] $C_{24}H_{32}KO_6$ requires 455.18360. Found: 455.18737; λ_{max}(MeOH)/nm 303 (ε/dm^3 mol^{-1} cm^{-1} 5980), 276 (10 480) and 229 (18 960). Inclusion of solvent molecules in the oily compound and the chemical sensitivity of DCOOH did not allow us to obtain a good elemental analysis.



1-[(4-Ethoxy-3-methoxy)phenylethan-1-one MCOET. Using a similar experimental procedure as before for the preparation of 7, MCOET was obtained from acetovanillone as pale yellow crystals (80%), mp 81 °C, δ($CDCl_3$, 60 MHz) 1.5 (3 H, t), 2.50 (3 H, s), 3.95 (3 H, s), 4.2 (2 H, q) and 6.7–7.8 (3 H, m); ν_{max}(KBr)/cm^{-1} 3060, 2990, 2920, 2880, 2820, 1670, 1590, 1500, 1480, 1440, 1400, 1390, 1350, 1330, 1280, 1250, 1210, 1170, 1130, 1070, 1030, 980, 940, 900, 870, 830, 800, 770 and 630; λ_{max}(MeOH)/nm 303 (ε/dm^3 mol^{-1} cm^{-1} 6260), 273.5 (8630) and 227.5 (14 960).

1-[(4-Hydroxy-3-methoxy)phenylethan-1-ol MREOH. To a solution of acetovanillone (2 g, 11.1 mmol) in ethanol (50 cm^3) was added sodium borohydride (850 mg, 22.2 mmol). The mixture was stirred for 3 h at room temperature and then acidified with dilute hydrochloric acid. Extraction with methylene chloride and usual work-up of the organic phase afforded, after purification by chromatography on silica gel [methylene chloride–ethyl ether (9:1 v/v)] MREOH as an oil (74%), δ($CDCl_3$; 60 MHz) 1.2 (1 H, s), 1.4 (3 H, t), 3.8 (3 H, s), 4.8 (1 H, q), 6.4 (1 H, s) and 6.6–7.2 (3 H, m); ν_{max}(KBr)/cm^{-1} 3400, 2940, 1600, 1510, 1450, 1420, 1360, 1270, 1230, 1150, 1120, 1070, 1030, 1010, 970, 910, 850, 800 and 770; *m/z* 168 (46%, M^+), 151 (100), 137 (6) and 125 (5); λ_{max}(MeOH)/nm 279 (ε/dm^3 mol^{-1} cm^{-1} 3270) and 228 (7220).

Preparative irradiation

A solution of 5 mg of MCOET in 5 cm^3 of THF (concentration: 5.15×10^{-3} mol dm^{-3}) was irradiated 4 h at 320 nm in a cell (1 mm path length) in several portions (0.3 cm^3 each run). After evaporation of the solvent, the residue was dissolved in methanol and separated by semi-preparative HPLC (reversed-phase: Kromasil C_{18} 5 µm, 25 cm length, 1 cm internal diameter, eluent methanol). The fractions were analysed by LSIMS ionization mass spectroscopy. Non-quantitative UV absorption spectra were also recorded for confirmation of the structure of the irradiating mixture. t_R 7.1 min; *m/z* 196 (100%, $M^{+\cdot}$); t_R 7.8 min; *m/z* 195 [100%, $(M + H)^+$]; t_R 8.5 min; *m/z* 249 [100%, $(M + H)^+$], 195 (100); t_R 9.0 min; *m/z* 249 [100%, $(M + H)^+$], 195 (100).

Acknowledgements

We acknowledge the *Groupement de Recherche 'Papiers et Dérivés (CNRS, CTP Grenoble)'* and the Commission of the European Communities (Forest Program Contract No. MA2B0018) for financial support. We are indebted to Dr R. Bonneau for his valuable assistance in the flash photolysis work.

References

1 C. Heitner, *ACS Symp. Ser.*, 1993, **531**, 2.

2 (*a*) K. P. Kringstad and S. Y. Lin, *Tappi*, 1970, **53**, 2296; S. Y. Lin and K. P. Kringstad, *Norsk Skogind.*, 1971, **25**, 252.

3 G. Brunow and B. Eriksson, *Acta Chem. Scand.*, 1971, **25**, 2779.

4 I. Forsskåhl, Thesis, Helsinki, Finland, 1985.

5 G. Brunow and M. Sivonen, *Paperi ja Puu*, 1975, **23**, 215.

6 J. Gierer and S. Y. Lin, *Svensk Papperstidn.*, 1972, **75**, 233.

7 (*a*) A. Castellan, P. Girard and C. Vanucci, *J. Wood Chem. Technol.*, 1988, **8**, 73; (*b*) C. Vanucci, P. Fornier de Violet, H. Bouas-Laurent and A. Castellan, *J. Photochem. Photobiol. A: Chem.*, 1988, **41**, 251; (*c*) A. Castellan, N. Colombo, C. Cucuphat and P. Fornier de Violet, *Holzforschung*, 1989, **43**, 179.

8 W. U. Palm, H. Dreeskamp, H. Bouas-Laurent and A. Castellan, *Ber. Bunenges.*, 1992, **96**, 50.

9 (*a*) J. C. Scaiano, J. C. Netto-Ferreira and V. Wintgens, *J. Photochem. Photobiol. A: Chem.*, 1991, **59**, 265; (*b*) J. A. Schmidt, A. B. Berinstain, F. de Rege, C. Heitner, L. J. Johnston and J. C. Scaiano, *Can. J. Chem.*, 1991, **69**, 104.

10 S. Omori, R. C. Francis and C. W. Dence, *Holzforschung*, (Suppl.) 1991, **45**, 93.

11 C. Jaeger, A. Nourmamode and A. Castellan, *Holzforschung*, 1993, **47**, 375.

12 B. Tadensg, *Synth. Commun.*, 1985, 76.

13 R. Mörck and K. P. Kringstad, *Holzforschung*, 1985, **39**, 109.

14 (*a*) J.-P. Desvergne, N. Bitit, A. Castellan, M. Webb and H. Bouas-Laurent, *J. Chem. Soc.*, *Perkin Trans. 2*, 1988, 1885; (*b*) A. Castellan, L. Kessab, S. Grelier, A. Nourmamode, M. Cotrait and P. Marsau, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 953.

15 (*a*) E. J. Baum, J. S. K. Wan and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, 1966, **88**, 2652; P. J. Wagner, A. E. Kemppainen and H. N. Schott, *J. Am. Chem. Soc.*, 1973, **95**, 5604.

16 A. Castellan, A. Nourmamode, C. Noutary, C. Belin and P. Fornier de Violet, *J. Wood Chem. Technol.*, 1992, **12**, 19.

17 A. Castellan, N. Colombo, C. Vanucci, P. Fornier de Violet and H. Bouas-Laurent, *J. Photochem. Photobiol. A: Chem.*, 1990, **51**, 451.

18 H. Lutz, E. Breheret and L. Lundquist, *J. Phys. Chem.*, 1973, **77**, 1758.

19 A. Castellan, A. Nourmamode, P. Fornier de Violet, N. Colombo and C. Jaeger, *J. Wood Chem. Technol.*, 1992, **12**, 1.

20 N. A. Weir, J. Arct, A. Ceccarelli and A. Siren, *Eur. Polym. J.*, 1994, **30**, 701.

21 S. Lazare, R. Lapouyade and R. Bonneau, *J. Phys. Chem.*, 1984, **88**, 18.

22 J. Fatiadi, *Synth. Org. Chem.*, 1976, **26**, 681.

Paper 5/06903C
Received 28*th November* 1995
Accepted 8*th January* 1996