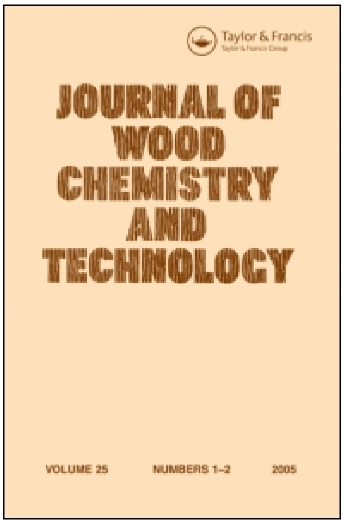

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

A Photoyellowing Simulation of Bleached High Yield Wood Pulp by Lignin Models Included in a Solid Carbohydrate Matrix

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To cite this Article Castellan, Alain , Girard, Philippe and Vanucci, Corinne(1988) 'A Photoyellowing Simulation of Bleached High Yield Wood Pulp by Lignin Models Included in a Solid Carbohydrate Matrix', Journal of Wood Chemistry and Technology, 8: 1, 73 — 90

To link to this Article: DOI: 10.1080/02773818808070671

URL: http://dx.doi.org/10.1080/02773818808070671

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 8(1), 73-90 (1988)

A PHOTOYELLOWING SIMULATION OF BLEACHED HIGH YIELD WOOD PULP BY LIGNIN MODELS INCLUDED IN A SOLID CARBOHYDRATE MATRIX.

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ABSTRACT

A series of lignin model molecules was prepared, adsorbed and grafted (for the most appropriate one) on to bleached chemical pulp . The rates of brightness reversion of these solid materials under simulated solar light exposure were established and compared to that of bleached mechanical pulp (containing lignin). 4-hydroxy-3-methoxy acetophenone (acetovanillone or acetoguaiacone) 1 and 3,5-dimethoxy-4-hydroxy acetophenone (acetosyringone) both incorporating α-carbonyl and phenolic functions which have been claimed essential for an efficient coloration, did not prove to be very active in the solid state. In contrast, α-carbonyl β-O-4 and β-1 structures with whether phenolic function or not, display an intense yellowing in this medium, and mimic well the brightness reversion of bleached mechanical pulp (especially the non phenolic β-O-4 chromophore adsorbed and grafted). These results are in contrast with those found in liquid ethanolic solution where acetovanillone 1 (conc.=10^{-2}M) and the α-carbonyl 4- O-methylated β-O-4 dimer 3 (conc.=3.7×10^{-3}M) were shown to undergo a similar yellowing. Inter and intramolecular mechanisms were put forward to explain this difference. Moreover, the reduction of the carbonyl chromophore into benzyl alcohol appears to prevent discoloration to some extent. However, all the studied structures were found light sensitive, even the 4-O-methylated α-O-4 dimer <u>11</u> which contains neither carbonyl nor phenolic groups.

INTRODUCTION

There is an increasing trend towards the use of bleached high yield wood pulps in the paper industry [1]. Unfortunately, their development is partly restricted by their yellowing under light exposure. The latter was attributed to the photoreactivity of lignin in the presence of oxygen [2].

It was previously shown that phenolic and α-carbonyl groups are mainly responsible for the discoloration of lignin and lignin model molecules in solution [3,4]. A mechanism involving hydrogen abstraction from phenol by excited triplet carbonyl groups leading to phenoxy radicals has been proposed [4]. These radicals are able to add ground state molecular oxygen to generate colored products such as quinones [5]. Later on this hypothesis was discarded in favor of a singlet oxygen mechanism [6]. As a matter of fact, in the highly viscous solid medium, the occurrence of efficient encounter between the two reactive sites (the carbonyl triplet and phenolic hydrogen) appears to be very limited [6]. Powerful oxidizing and highly diffusible species such as excited singlet oxygen seem to be more suitable for the degradation process [6].

Experiments conducted in this laboratory on a series of O-methylated lignin model dimers [7], irradiated in *liquid aqueous solutions*, have shown that etherification does not suppress the yellowing of α-O-4 and α-carbonyl β-O-4 compounds, even in *rigo-*

rously degassed media. Thus, in solution, the presence of ground state oxygen does not appear to be essential to induce a photodiscoloration. Moreover, very recent results published by M. Neumann, indicate that singlet oxygen is involved only after appearance of some photoproducts (such as quinones which display a high absorption in the visible range), which are able to sensitize its formation [8]. The photodegradation of lignocellulosic polymers is so far a subject where extensive experimental work remains [9].

In connection with the study of the photodegradation of lignin, some protection against the photoyellowing has been proposed either by masking the phenols as esters or ethers, and/or by reducing the carbonyl moiety [3,10-12]. However, except for borohydride reduction of soluble lignin followed by catalytic hydrogenation [11], none of the proposed treatments has turned out to stabilize completely the polymer against photodiscoloration.

In the present communication, we report a simulation of the rate of brightness loss (under simulated solar light exposure) of bleached mechanical pulp, performed on a series of lignin model monomers and dimers (Fig.1) adsorbed and grafted (for the most appropriate one) on to a bleached chemical pulp. This work is expected to bring new insight into the intricate mechanism of the photoinduced brightness reversion of lignocellulosic materials, especially to underline *the influence of the solid matrix* which has not been examined so far.

EXPERIMENTAL

A) Materials

4-hydroxy-3-methoxyacetophenone (acetovanillone) and 3,4-dimethoxy-4-hydroxy acetophenone (acetosyringone) were purchased from Aldrich Company.

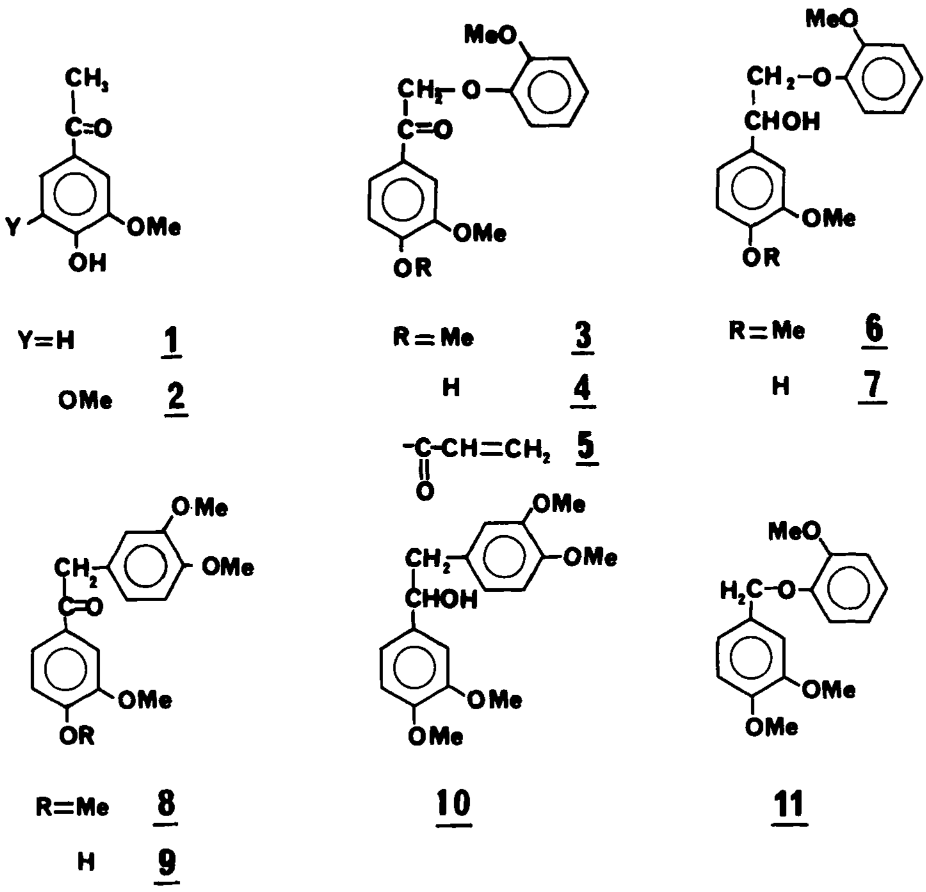

Figure 1 : Lignin model compounds used in the study.

3,4-dimethoxy-α-(2'-methoxyphenoxy)acetophenone (3) was prepared from α-bromoacetoveratrone and guaiacol in the presence of K_2CO_3 in dry acetone. Yield:69% ; mp=94°C (Lit.:93.5-94.5 [13]).

4-hydroxy-3-methoxy-α-(2'-methoxyphenoxy)acetophenone (4) was synthesized similarly to compound 3 from 4-acetoxy-3-methoxy-αbromoacetophenone and 2-methoxyphenol (guaiacol) followed by saponification (K_2CO_3) in methanol. Yield : 62% ; mp=92°C (lit. 92-93°C [13]).

3,4-dimethoxy-α-(3',4'-dimethoxyphenyl)acetophenone (Desoxyveratroine (8)) was obtained by Friedel-Crafts reaction of 3-4-dimethoxyphenylacetyl chloride with 1,2 dimethoxy benzene (veratrole) in a CH_2Cl_2/CS_2 mixture (2v/3v). Yield : 64% ; mp=107°C (lit.:107°C [14]).

1-(3'-methoxy-4'-hydroxyphenyl)-2-(3",4"-dimethoxyphenyl)-ethanone (9). The Friedel-Crafts reaction of 3,4-dimethoxyphenylacetyl chloride with 1-methoxy 2-isopropyloxybenzene, using the procedure described for 8, gives 9 directly . Yield : 41% ; mp=135°C.

^{1}H NMR ($CDCl_3$) δ ppm : 6.62-7.73 (m,ArH, 6H); 6.13 (b.s., OH, 1H); 4.06 (s, CH_2, 2H); 3.82 (s, OCH_3, 3H); 3.75 (s, OCH_3, 6H).

^{13}C NMR ($CDCl_3$) δ ppm : 44.6 (Cβ); 55.9 (OCH_3); 127.7 ; 111.0 ; 147.0, 150.9 ; 114.2 ; 124.2 (C_1 to C_6 respectively); 129.4 ; 111.5 ; 149.1 ; 148.0 ; 112.7 ; 121.6 ($C_{1'}$ to $C_{6'}$ respectively); 197 (α C=O).

IR ν max (KBr) : 3380, 3000, 2950, 2900, 2840, 1660, 1600, 1590, 1520, 1470, 1455, 1430, 1380, 1325, 1270, 1195, 1165, 1130, 1025, 875, 815, 715 cm^{-1}.

MS (70 eV) m/z (rel. int.) : 302 (M^+, 8%); 151 ($[3,4\text{-}(CH_3O)_2\text{-}\Phi\text{-}CH_2]^+$ and $[3(CH_3O)4\text{-}(OH)\text{-}\Phi\text{-}CO]^+$,100%); 123 ($[3\text{-}(CH_3O)4\text{-}(OH)\text{-}\Phi]^+$, 7%).

UV (EtOH) λ_{max} nm (ε l mol^{-1} cm^{-1}) : 307 (9990) ; 278 (12780) ; 230 (22380).

The benzyl alcohols 6, 7 and 10 were prepared by $NaBH_4$ reduction (ethanol) of the corresponding α-carbonyl dimers 3, 4 and 8.

1-(3',4'-dimethoxyphenyl)-2-(2"-methoxyphenoxy)ethanol (6). Yield : 77% mp=132.5 °C (lit. 133-134°C [15]).

1-(4'-hydroxy 3'-methoxyphenyl)-2-(2"-methoxyphenoxy)ethanol (7). Yield : 75% ; mp=130°C (Lit. 129-130°C [15]).

bis 1,2-(3',4'-dimethoxyphenyl)ethanol (10). Yield : 80%; mp=110°C.

^1H NMR ($CDCl_3$) δ ppm : 6.56-6.93 (m, ArH, 6H); 4.76 (t (J=8,4 Hz), -αCH-, 1H); 3.83 and 3.78 (s, $-OCH_3$, 12H); 2.93 (d (J=8,4Hz), $-\beta CH_2$, 2H); 2.33 (s large, -OH, 1H).

IR ν_{max} (KBr) : 3500, 3005, 2940, 2840, 1605, 1590, 1515, 1465, 1420, 1260, 1235, 1155, 1140, 1030, 910, 810, 725 cm^{-1}.

MS m/z (chemical ionization, NH_3) : 336 ($[M,NH_4]^+$, 20%); 301 (100%).

UV (ethanol) λ_{max} nm (ε $1.mol^{-1}cm^{-1}$) : 279 (5810); 230 (16280).

3,4-dimethoxy-α-(2'-methoxyphenoxy)toluene 11 was synthesized according to a procedure described by Ciaramitaro [16] for similar compounds, using 3,4-dimethoxy-α-bromotoluene, guaiacol and K_2CO_3 in dry acetone. Yield : 30% ; mp=81°C.

^1H NMR ($CDCl_3$) δ ppm : 6.93-7.4 (m, ArH, 7H); 5.2 (s, CH_2, 2H); 3.93 (s, OCH_3, 9H).

IR ν_{max}(NaCl): 3000, 2940, 2840, 1590, 1515, 1500, 1460, 1450, 1420, 1380, 1330, 1250, 1180, 1160, 1140, 1130, 865, 810, 745 cm^{-1}.

MS (70eV) m/z (rel. int.) : 274 (M^+, 2%); 151 ($[3,4\ (CH_3O)_2-\Phi-CH_2]^+$, 100%), 123 ($[(CH_3O)-\Phi-O]^+$, 1%), 107 (6%).

UV (ethanol) λ_{max} nm (ε 1 mol^{-1} cm^{-1}) : 277 (5630); 228 (15920).

Pulps : The chemical pulp used for the study, graciously provided by "La Cellulose du Pin", was an industrial ammonium bisulfite (maritime pine) pulp bleached by a multistage CEHD sequence. Stone groundwood pulp (spruce) bleached with hydrogen peroxide, kindly furnished by Dr. Lachenal (Centre Technique du Papier, Grenoble) was taken as sample for high yield pulp sheets ($100 g/m^2$).

Acrylate 5 grafted on bleached chemical pulp :

4-(3-methoxy-α-[2'-methoxyphenoxy]acetophenone) acrylate 5 was prepared by reaction (room temperature; nitrogen atmosphere; magnetic stirring) of the sodium salt of 4 (3g; 9.7 mmol) with acryloyl chloride (0.8mL; 9.8 mmol) in a mixture of dry solvents : THF (17 mL), cyclohexane (7 mL) and toluene (12.5 mL). After 3 hours of stirring, the inorganic precipitate was filtered and treated with 20mL of toluene. The organic phase was washed with water in order to eliminate the THF and was used in that state for the gratfing. To 500 mg of bleached bisulfite pulp dipped in distilled water (100 mL) under intense mechanical stirring, was added potassium persulfate (25mg) and ceric IV ammonium sulfate (30mg). The stirring was continued for 5 minutes more. Wet fibers incorporating the polymerisation initiators were obtained by filtration and were used in this moist condition for the grafting.

The grafting was carried out by reaction under efficient magnetic stirring (N_2 atmosphere) of the preceding fibers with the acrylate solution at 100°C for 70h. The grafted fibers, contaminated with a little quantity of sticky homopolymer, were isolated by filtration. The homopolymer was eliminated from the fibrous mat by successive dissolving in chloroform, acetone, methylene chloride, ethanol, water, ethanol and ether. The grafted fibers characterized by their infrared spectrum (fig.2) include 10% of the acrylate component . This value was estimated by weighing the dimer 4, isolated after saponification of a known amount of fibers with K_2CO_3 in methanol.

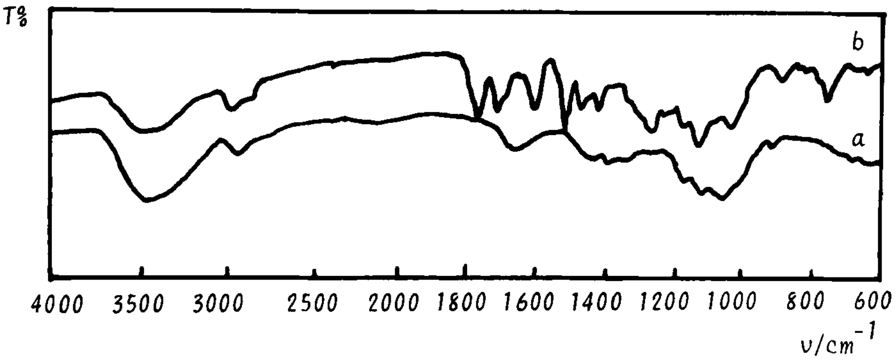

Figure 2 : *Infrared spectra of bleached pine bisulfite pulp before (a) and after (b) acrylate (5) grafting. The IR spectra of the pulp (2-3mg) in KBr (200 mg) were run as discs.*

Due to the brittleness of the grafted fibers, sheets were made by filtration of an homogeneous ethanolic suspension of the fibers on a filter paper and were dried at room temperature. The rate of photoyellowing was determined using this two-layer-material.

B) Rate of brightness loss

a) paper samples

Sheets (4.5 x 4.5 cm, 1.7g) of bleached chemical pulp, were dipped for 5 minutes into a solution (ethanol or methylene chloride) of the studied compounds (conc. ≈ 7×10^{-2}M); the solvent was then evaporated under a warm air stream (60°C). The weight percents of the model compounds on the dry paper were estimated by weighing the remaining model compounds after solvent evaporation. The concentrations used for the rate studies are reported in Table 1.

TABLE 1

Molar amount (M) of adsorbed compounds on bleached chemical papers and weight percentages (P) relative to oven-dried sheets (≈ 1.7g). Molecular weights of model compounds are indicated in parenthesis.

COMPOUNDS	1 (166)	2 (196)	3 (302)	4 (288)	6 (304)	7 (290)	8 (316)	9 (302)	10 (318)	11 (274)
M (10^{-4} mole)	1.6	2.3	1.6	1.5	1.4	1.2	1.3	1.2	1.2	1.6
P (%)	1.5	2.6	2.9	2.5	2.5	2.0	2.3	2.2	2.3	2.5

b) Rate of brightness reversion.

The paper sheets were comparatively exposed (temperature ≈ 25°C) to an homogeneous light beam of a Xenon lamp (150W), the wavelengths below 300 nm being eliminated with a borosilicate glass filter (in order to simulate emission from the sun). Brightness indices were measured as a function of the irradiation time with a Zeiss Elrepho apparatus.

The UV spectra of the model compound in solution were measured on a Cary 219 instrument.

RESULTS AND DISCUSSION

The UV spectra of the studied lignin model compounds presented in figure 3 underline the key role played by the α-

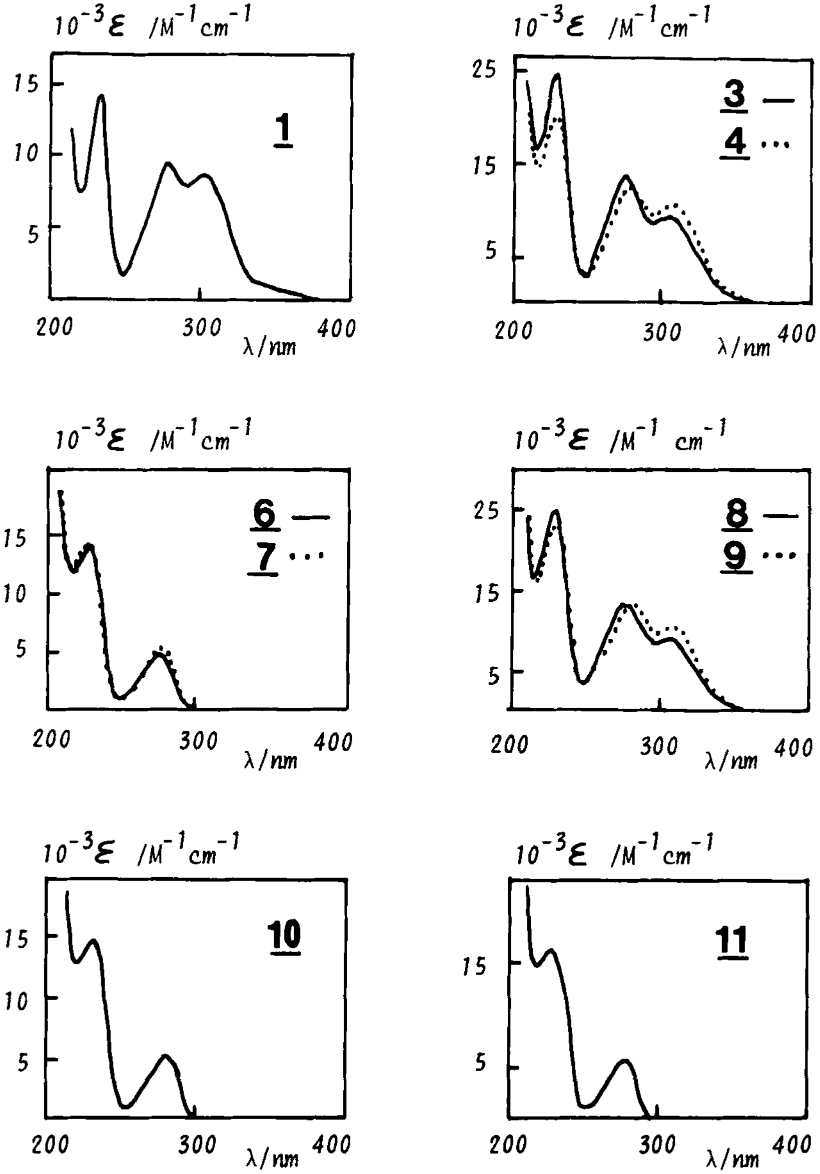

***Figure 3** : U.V. absorption spectra in ethanol of the lignin model compounds under study.*

carbonyl functions in the bathochromic shift of the benzenoid chromophore absorption, above 300 nm, where the sunlight is more intense.

In figure 4 are depicted the rates of brightness loss under comparative simulated solar light exposure of a/ adsorbed lignin monomers (1,2) and dimers (3, 4, 6-11) on bleached delignified pulp, b/ a "synthetic" high yield wood pulp paper formed by an α-carbonyl β-O-4 acrylate (5) grafted on bleached chemical fibers, and c/ a bleached softwood mechanical pulp. In the same experimental conditions, the absence of yellowing, of the chemical pulp was noted.

Taking into account their electronic absorption spectra, the examined compounds can be classified into two categories :

a) α-carbonyl derivatives.

It is noteworthy that the model monomers acetovanillone 1 and acetosyringone 2, which are representative of softwood and hardwood lignins, do not undergo a significant discoloration within the investigated period. The large distance between the excited triplet carbonyl chromophore and the phenolic hydrogen, as previously suggested [6], could explain their low reactivity in the solid medium. However, one cannot dismiss the hypothesis that some interactions in the solid state such as hydrogen bonds between the carbohydrate hydroxy groups and the reactive centers (phenolic OH and/or carbonyl triplet), might suppress the photochemical reaction. Yet, an experiment conducted with acetovanillone on silylated papers displaying hydrophobic surfaces, did not show any increase in discolouration. This result is indicative of little or no involvement of this type of interaction in the photodegradation process.

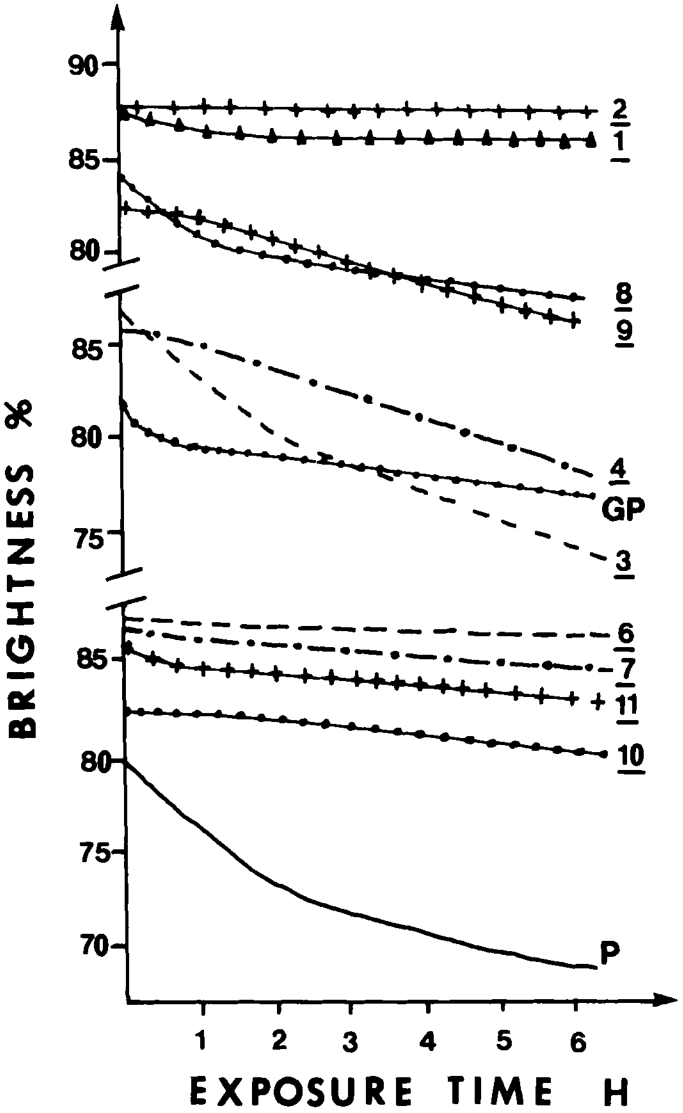

Figure 4 : *Rate of yellowing under simulated solar light of adsorbed lignin model monomers (1, 2) and dimers (3, 4, 6-11) on delignified paper of bleached softwood mechanical paper (P), and of grafted paper (GP) with acrylate 5.*

TABLE 2

Compared photoyellowing of compounds 1 and 3 in aerated ethanolic solution (λ irradiation = 342 nm, T = 25°C) : a) before irradiation ; b) after 3 hours of irradiation.

COMPOUND	1	3
Abs(342)[a]	2.15	2.15
Conc.,M	10^{-2}	3.7×10^{-2}
Abs(457)[b]	0.07	0.06

Moreover, the observation that 1 and 3 undergo a similar yellowing in aerated ethanolic solution (see Table 2), strengthens the hypothesis concerning the importance played by the solid matrix in the photoyellowing. In the carbohydrate matrix, medium of high viscosity, the intermolecular process involved in the photodegradation of α-carbonyl monomers [5,17,18] should be more limited than the intramolecular one which is put forward for the α-carbonyl β-O-4 structures [19,20].

In contrast to the behaviour of the monomers 1 and 2, α-carbonyl β-O-4 and β-1 lignin model dimers display a rapid and intense yellowing, in the same maner as does the mechanical pulp. One notes that α-carbonyl β-1 structures have not so far been considered capable of inducing a strong coloration in lignin. Besides, the presence of free phenolic groups does not appear to be essential to cause a yellowing of the α-carbonyl β-O-4 and β-1 dimers. Moreover, the best simulation was observed for the 4-O-methylated compound 3, suggesting that this molecule is adequate for model studies.

The photochemical reactivity of 4-O-Methyl-α-carbonyl β-O-4 compounds was first studied by Gierer and Lin [19] but a thorough chemical analysis of the reaction products performed on 3 in this laboratory [20] under various experimental conditions (solution and solid, degassed or not), has stressed the importance of *the intramolecular β-aryl ether cleavage* as the primary step in the photochemical reaction of these molecules leading to guaiacyl and phenacyl radicals (figure 5). The radicals are *inter alia* rearranged into α-carbonyl β-1 phenolic dimers and colored oligomeric materials which confer the yellow aspect to the media. α-Carbonyl β-1 derivatives appear in some extend to be in the pathway to the formation of coloured oligomers [20]. This is in agreement with the rate of brightness loss observed. Studies of the photodegradation process of α-carbonyl β-1 dimers, as well as a structural analysis of the oligomeric materials, are in progress in this laboratory.

The covalent linkage created between the β-O-4 structure and the carbohydrate matrix in the "synthetic" high yield wood pulp including one chromophore, does not bring any major change to the yellowing kinetic rate, even if one notes a contraction in the brightness scale. This might be due to a lower absorption of the β-O-4 chromophores, the grafted fibers being in the bulk fibrous mat, whereas the absorbed models are mainly located at the surface of the sheet. Nevertheless, the yellowing obtained with the grafted material underlines once again the importance of the intramolecular primary step in the coloration process.

b) Non carbonyl derivatives

The reduction of the carbonyl chromophore brings a net stabilization against the yellowing. The UV spectra in this case,

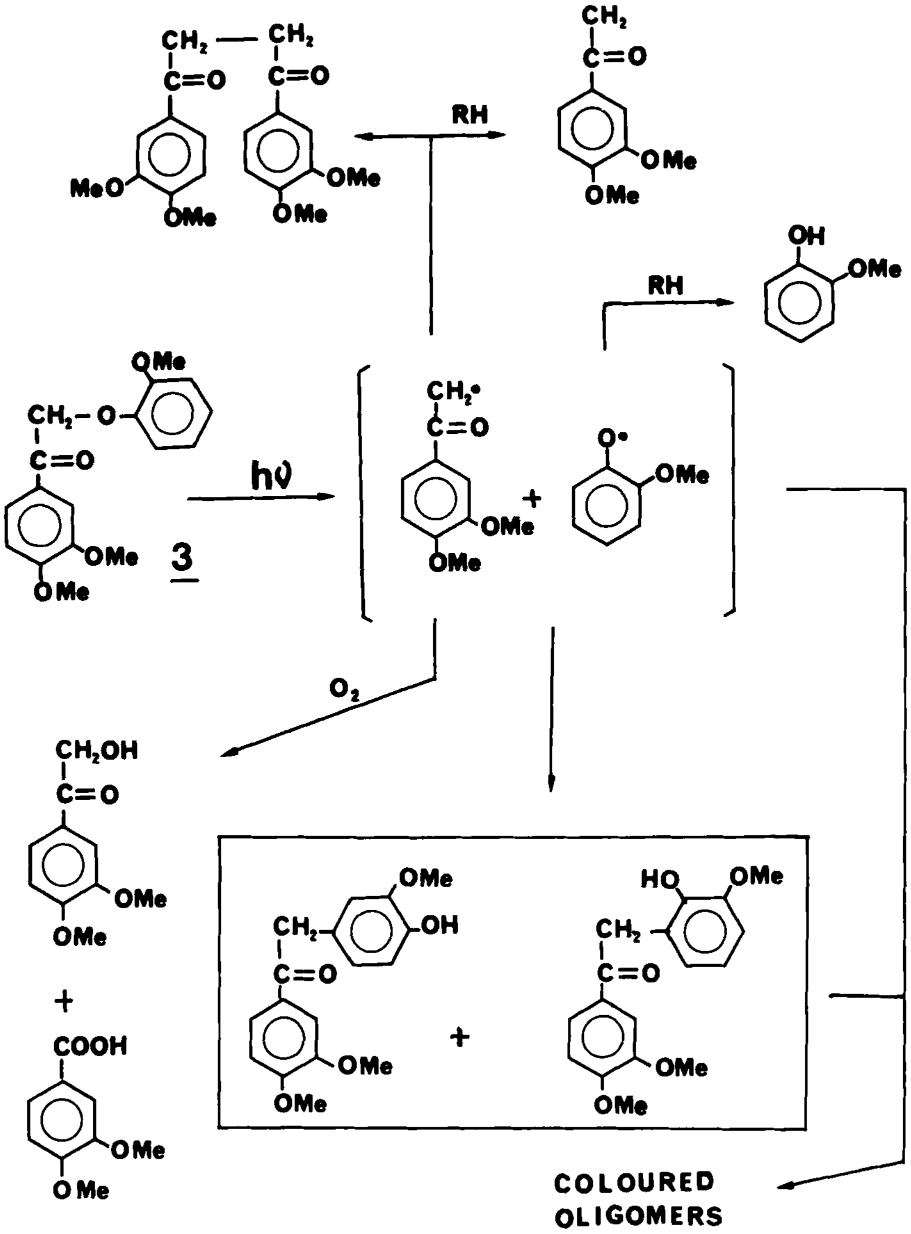

Figure 5 : Proposed degradation mechanism of 4-O-methylated α-carbonyl β-O-4 dimer 3 [20].

are shifted to shorter wavelengths ($\lambda \leq 300$ nm), where UV contribution of the sunlight is less. However, the observed slight yellowing is probably ascribable to a photooxidation of the benzylic alcohol into sunlight sensitive α-carbonyl derivatives by a mechanism involving an electron transfer process [7,21].

It is noteworthy that 4-O-methylated α-O-4 structures which contain neither carbonyl nor phenolic groups undergo a photoyellowing. It was shown elsewhere [22] that such molecules are photolysed by an intramolecular benzyl-aryl ether cleavage, leading ultimately to colored oligomeric materials.

CONCLUSION

The establishment of the rate of brightness reversion under simulated solar light exposure has revealed some features which could be considered surprising in the light of the already published literature. Monomeric molecules containing both α-carbonyl and free phenolic groups, such as acetovanillone and acetosyringone, do not undergo an efficient photoyellowing on the solid carbohydrate surface. The medium, preventing the intermolecular reaction, appears, in this case, to be one of the main responsible factors for the observed slight coloration. In contrast, α-carbonyl β-O-4 and β-1 dimer molecules display an intense yellowing in condensed media. It is noteworthy that the presence of phenolic groups is not essential to induce a significant photodiscoloration. An intramolecular photodegradation mechanism, not very dependent on medium viscosity, has been put forward to explain this difference. Moreover, even in the absence of α-carbonyl and phenolic groups in molecules such as benzylic alcohols and 4-O-methylated α-O-4 dimers, these derivatives were found to be sensitive to sunlight in the solid, although they do not strongly absorb over 300 nm.

Acknowledgements

Financial support and a thesis grant to C.V. from the Groupement Scientifique "Cellulose-Papier" (CNRS and Centre Technique du Papier, Grenoble) are gratefully acknowledged. We thank the "Institut du Pin" and "La Cellulose du Pin" for allowing us to use their equipment and for providing us with chemical fibers (C.P.). We are indebted to Dr Lachenal (C.T.P.) for his interest in this work and for furnishing of bleached mechanical pulp. We also thank Professor H.Bouas-Laurent for stimulating discussions. The assistance of Mr Sarrebeyroux in the preparation of some starting materials was appreciated.

REFERENCES

1. D.H. Breck and G.E. Styan, Tappi, 68, 40 (1985).
2. P. Nolan, J.A. Van den Akker and W.A. Wink, Paper Trade J., 121, 101 (1945).
3. G.J. Leary, Tappi, 51, 257 (1968).
4. K.P. Kringstad and S.Y. Lin, Tappi, 53, 658 and 2296 (1970).
5. K.P. Kringstad and S.Y. Lin, Norsk Shogindustri, 9, 252 (1971).
6. G. Gellerstedt and E. Petterson, Acta Chem. Scand., 29, 1005, (1975).
7. A. Castellan, C. Vanucci, J-P. Desvergne, H. Bouas-Laurent, M. Hauteville and M. Chadenson, C.R. Acad. Sc., 301, 21 (1985).

8. M.G. Neumann, R.A. De Groote, A.E. Machado, Polym. Photochem., 7, 401 (1986) and 7, 461 (1986).

9. Fourth International Symposium on Wood and Pulping Chemistry, Paris, April 27-30 (1987). Abstract 1, 309 ; 1,313 ; 1, 321 ; 2, 245 ; 2, 239.

10. R.P. Singh, Tappi, 49, 281 (1986).

11. S.Y. Lin and K. Kringstad, Tappi, 53, 1675 (1970).

12. G. Gellerstedt and E.L. Pettersson, Svensk Papperstid., 80, 15 (1977).

13. R. Brezny and V. Mihalov, Cell. Chem. Technol., 18, 575 (1984).

14. I. Allen and J.S. Buck, J. Am. Chem. Soc., 52, 310 (1930).

15. J. Gierer and I. Noren, Acta Chem. Scand. , 16, 1713 (1962).

16. D. Ciaramitaro and C. Steelink, Phytochem., 14, 543 (1975).

17. I. Forsskahl, J. Photochem., 27, 363 (1984).

18. Ph. Girard, Thesis, Université de Bordeaux I, (1986).

19. J. Gierer and S. Lin, Svensk Papperstid.,75, 233 (1972).

20. C. Vanucci, Ph. Fornier de Violet, H. Bouas-Laurent and A. Castellan, J. Photochem. Photobiol. A: Chem. in the press.

21. J. Santamaria, P. Gabillet and L. Bokobza, Tetrahedron Letters, 25, 2139 (1984).

22. A. Castellan, C. Vanucci and H. Bouas-Laurent, Holzforschung, 41, 231 (1987).