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Routes of degradation of β-*O*-4 syringyl and guaiacyl lignin model compounds during photobleaching processes

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Abstract

The photolysis of guaiacyl and syringyl β-*O*-4 lignin model compounds (I, II, III and IV) with a phenol or α-*O*-4 substituted in the phenacyl moiety was done by three different methods, designed to perform the photobleaching of lignocellulosics. The photolysis systems were carried out in alkaline methanolic solution (pH ∼ 11), and consisted in: (a) H_2O_2, (b) methylene blue (MB)/O_2 and (c) TiO_2. The fragments produced in the reactions were analyzed by mass spectrometry–gas chromatography technique. The results show that the reaction is dependent on the substituent in the phenacyl moiety. The most important route for the degradation mechanism seems to be the incorporation of the hydroxyl radical in the aromatic rings. Semi-empirical calculations of the charge distribution over the atoms in the model compounds show that this parameter is important to decide the reaction mechanisms. For the unprotected phenolic model compound the production of phenolic fragments is higher than in the labile substituted α-*O*-4 model compound. On the other hand, the photodegradation of the model compound (IV) using method (a) yielded coniferyl alcohol as the principal product. The processes (a) and (c) showed to be the most aggressive for the studied compounds.

Keywords: Photobleaching; Lignin model compounds; Oxygen species; Photocatalysis

1. Introduction

The removal of lignin from lignocellulosic materials is an essential step for the production of paper, defining its applicability and final price [1,2]. The presence of certain chromophores in the remaining lignin fragments will contribute to the posterior yellowing of the bleached pulp or paper [3]. The efficient removal of these fragments present on the fibers, or the use of different kinds of stabilizers has been the aim of the work of many researches, although it can be a difficult task [4–15]. On the other hand, the preservation of the mechanical properties of bleached cellulose must be persecuted if quality is the final objective of the bleaching process.

We have studied the development of alternative bleaching processes, based on photochemical reactions. The first one involves the decomposition of H_2O_2 by ultraviolet light under alkaline pH (∼11). The exposition of hydrogen peroxide to UV light results in the generation of oxygen active species capable to react with structural elements of lignin [16,17].

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet$$

$$H_2O_2 + HO^\bullet \rightarrow HOO^\bullet + H_2O$$

$$HO^\bullet + HOO^\bullet \rightarrow {}^1O_2 + H_2O$$

$$H_2O_2 + HO^- \rightarrow HOO^- + H_2O$$

$$O_2^{\bullet -} + HO^\bullet \rightarrow HO^- + {}^1O_2$$

$$HOO^- + HO^\bullet \rightarrow O_2^{\bullet -} + H_2O$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow HO^\bullet + HO^- + {}^1O_2$$

Under these conditions, important reactive species such as hydroperoxy and hydroxyl radicals, anion superoxide and probably singlet oxygen are formed, inducing degradative steps in the lignocellulosic materials.

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The second process is based on the generation of singlet oxygen by photosensitization under alkaline pH. In this process, methylene blue (MB) has been used as photosensitizer. Its excitation, in the presence of molecular oxygen results in the formation of singlet oxygen.

$$^{1}(\mathrm{MB}) + h\nu \rightarrow {}^{3}(\mathrm{MB})^{*}$$

$$^{3}(\mathrm{MB})^{*} + {}^{3}\mathrm{O}_2 \rightarrow {}^{1}(\mathrm{MB}) + {}^{1}\mathrm{O}_2^{*}$$

The quenching of singlet oxygen by other species present in the solution, like hydroxy ions, generates hydroxyl radicals and superoxide anions as the predominant oxygen active species [18,19].

The third process involves the application of photocatalysis [20–23], a technique initially proposed by Fujishima and coworkers [24,25] in 1969. In this process, light of appropriate energy promotes an electron from the valence band to the conduction band, generating an electron (e^-)/hole (h^+) pair that can induce the mineralization of organic compounds [24–30] and reduce some metallic ions [31]. Machado and coworkers [20,22] reported efficient breakdown of lignin and lignin model compounds, during the bleaching of cellulose pulps by photocatalysis mediated by TiO_2, using UV light and oxygen. Hydroxyl radicals can be generated by the strong oxidative potential of the hole in presence of water and/or alkali as shown below in the reaction scheme.

$$\mathrm{TiO_2} + h\nu \rightarrow \mathrm{TiO_2}(\mathrm{e^-}/\mathrm{h^+})$$

$$\mathrm{TiO_2}(\mathrm{h^+}) + \mathrm{OH^-} \rightarrow \mathrm{TiO_2} + \mathrm{HO^{\bullet}}$$

$$\mathrm{TiO_2}(\mathrm{e^-}) + \mathrm{O_2} \rightarrow \mathrm{TiO_2} + \mathrm{O_2}^{\bullet -}$$

$$\mathrm{TiO_2}(\mathrm{h^+}) + \mathrm{L} \rightarrow \mathrm{TiO_2} + \mathrm{L}^{\bullet +}$$

$$\mathrm{OH^{\bullet}} + \mathrm{O_2}^{\bullet -} \rightarrow \mathrm{OH^-} + {}^{1}\mathrm{O_2}$$

where L is lignin.

In this work, we discuss the possible routes for lignin degradation based on these three photochemically mediated processes, using β-*O*-4 lignin model compounds.

2. Experimental

The photochemical degradation of four lignin model compounds, two guaiacyl and two syringyl (10^{-3} mol dm^{-3}), was evaluated considering three different photochemical processes, used to bleach lignocellulosics:

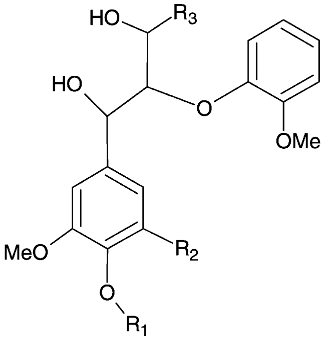
(a) Oxygen active species (OAS) generated by photoassisted and thermal degradation of hydrogen peroxide (0.88 mol dm^{-3}), under alkaline pH.
(b) Singlet oxygen, generated by photosensitization, using methylene blue (4.5×10^{-5} mol dm^{-3}).
(c) Photocatalytical process using TiO_2 (1% (w/w)).

In the three processes, two 400 W mercury lamps were used as irradiation source. The temperature in the reactional system was maintained at approximately 302 K. A boron-silicate glass reactor was used to input an effective wavelength irradiation higher than 320 nm. Considering this, in the first and third processes, direct photolysis of the lignin model compounds occurs concomitantly with the process induced by the action of oxygen active species. For the second process, a $NaNO_2$ solution (80/g dm^{-3}) was used as a filter to cut off the UV energy components below 400 nm.

In all experiments, methanol was the solvent in order to allow the solubilization of the model compounds and alkalinization of the solutions.

Fig. 1 shows the structure of the models used in this study.

The compounds were synthesized by Castellan and co-workers in the Laboratoire de Chimie de Substances Végétales, Institut du Pin, Université Bordeaux 1, by a method developed by Nakatsubo and Higuchi [26] with modifications made by Ralph et al. [28]. The characterization



(I) 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol

(II) 1-(4-benzyloxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol

(III) 4-(4-benzyloxy-3-methoxyphenyl)-3-(2-methoxyphenoxy)butane-1,2,4-triol

(IV) 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol

Fig. 1. Lignin model compounds studied: (I) 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanol; (II) 1-(4-benzyloxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenyl)-3-hydroxy-1-propanol; (III) 1-(4-benzyloxy-3-methoxyphenyl)-2-(2-methoxyphenyl)-3-hydroxymethyl-4,1-butanediol; (IV) 1-(3,4-dimethoxyphenyl)-2-(2′-methoxyphenoxy)-1,3-dihydroxypropane.

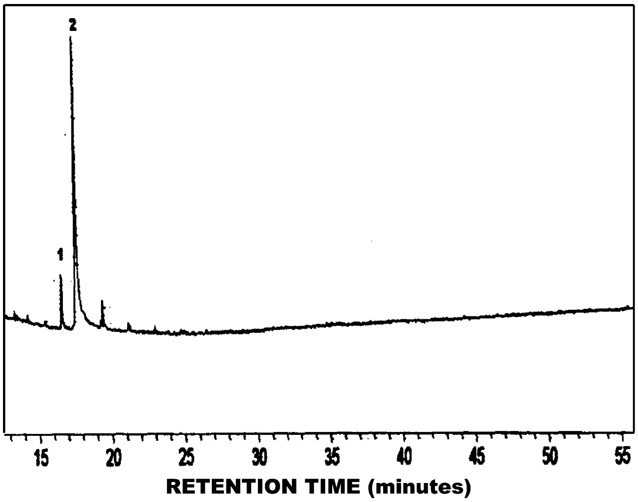


Fig. 2. Gas chromatogram of the degradation products of model IV: starting material (1); coniferyl alcohol (2).

was done by NMR ^{1}H and ^{13}C. Data for compounds III and IV were previously described [18], while the spectroscopic NMR data for compounds I and II are showed below.

2.1. Model (I)

NMR ^{1}H (250 MHz, CDCl$_3$): δ (ppm): 3.31—singlet (1H) –O**H**; 3.75—singlet (6H) –OC**H**$_3$ (syringyl ring); 3.81—singlet (3H) –OC**H**$_3$ (guaiacyl ring); 3.60–4.20—multiplet (4H) –$^\gamma$C**H**$_2$, –$^\beta$C**H**–, –O**H**; 4.97—doublet (1H) –$^\alpha$C**H**–; 5.10—singlet (2H) –OC**H**$_2$Ar; 6.66–7.50—multiplet (6H) Ar**H**.

NMR ^{13}C (63 MHz, CDCl$_3$): δ (ppm): 56.33 (O**C**H$_3$), 56.86 (O**C**H$_3$), 60.83 (**C**$_\gamma$), 73.14 (**C**$_\alpha$); 75.14 (O**C**H$_2$Ar), 86.87 (**C**$_\beta$), 102.84 (**C**$_2$ and **C**$_6$), 113.85 (**C**$_{2'}$); 120.87 (**C**$_{5'}$), 121.65 (**C**$_{1'}$), 122.27 (**C**$_{6'}$), 127.85 (**C**$_4$); 128.12 (**C**$_{2''}$, **C**$_{4''}$ and **C**$_{6''}$), 128.16 (**C**$_{3''}$ and **C**$_{5''}$), 137.81 (**C**$_{1''}$); 146.85 (**C**$_{4'}$), 151.27 (**C**$_{3'}$), 153.58 (**C**$_3$ and **C**$_5$).

2.2. Model (II)

NMR ^{1}H (250 MHz, CDCl$_3$): δ (ppm): 3.60–3.80—multiplet (10H) –OC**H$_3$**, –O**H**; 4.15—singlet (3H) –CO$_2$C**H$_3$**; 4.72 and 5.14—system AB (2H) $^\alpha$C**H**–$^\beta$C**H** ($^3J_{\mathrm{AB}}$ = 5, 3 Hz); 4.92—singlet (2H) –OC**H$_2$**Ar; 6.60–7.60—multiplet (11H) Ar**H**.

NMR ^{13}C (63 MHz, CDCl$_3$): δ (ppm): 55.86 (O**C**H$_3$), 56.33 (O**C**H$_3$), 61.34 (COO**C**H3), 74.14 (**C**$_\alpha$); 83.74 (**C**$_\beta$), 104.91 (**C**$_2$ and **C**$_6$), 112.18 (**C**$_{2'}$), 118.86 (**C**$_{5'}$); 121.14 (**C**$_{1'}$), 123.92 (**C**$_{6'}$), 127.89 (**C**$_{4''}$), 128.19 (**C**$_{2''}$ and **C**$_{6''}$); 128.55 (**C**$_{3''}$ and **C**$_{5''}$), 131.99 (**C**$_4$), 134.78 (**C**$_1$), 137.88(**C**$_{1''}$); 146.85 (**C**$_{4'}$), 151.27 (**C**$_{3'}$), 152.57 (**C**$_3$ and **C**$_5$).

In order to analyze the photolysis products, the samples were concentrated by solvent evaporation at room

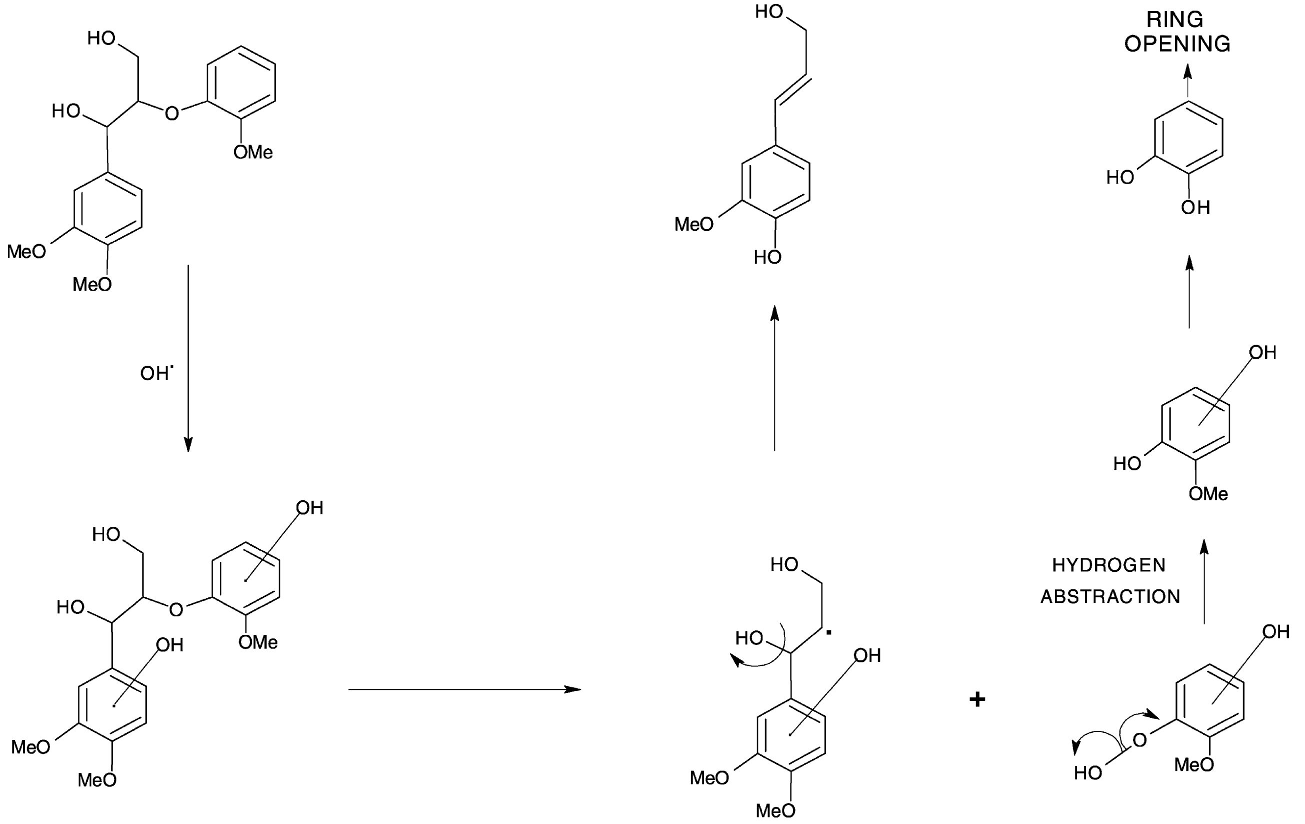
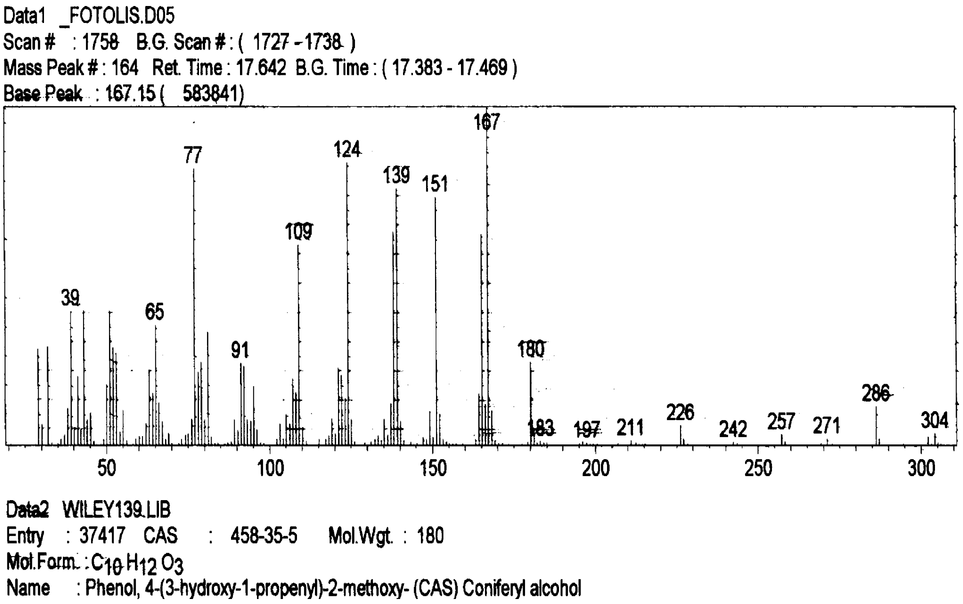


Fig. 3. Scheme proposed for the degradation of model compound (IV) by the action of hydroxyl radicals.



Data1 _FOTOLIS.D05
Scan # : 1758 B.G. Scan # : (1727 - 1738)
Mass Peak # : 164 Ret. Time : 17.642 B.G. Time : (17.383 - 17.469)
Base Peak : 167.15 (583841)

Data2 WILEY139.LIB
Entry : 37417 CAS : 458-35-5 Mol.Wgt. : 180
Mol.Form. : $C_{10}H_{12}O_3$
Name : Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy- (CAS) Coniferyl alcohol

Fig. 4. Mass spectrum presenting the observed fragmentation of the second peak, attributed to coniferyl alcohol, from gas chromatogram of the degradation products from model compound IV degradation mediated by hydroxyl radicals.

temperature, acidified (pH 3–4) with aqueous HCl and extracted with dichloromethane (∼3 ml). The separated organic phase was then dried at ambient temperature, dissolved in 100 μl of dry tetrahydrofuran (THF), and silylated with bis- (trimethylsilyl)-trifluoroacetamide (BSTFA) (50 μl) in the presence of pyridine (20 μl). The analysis of the photoproducts was performed by gas chromatography using a flame ionization detector (Shimadzu GC 14A equipped with a C-R4A Chromatopac data analyzer) or by CG–MS (Shimadzu, QP 5000 with a DB-5MS and a J W Scientific capillary column, 30 m length × 0.25 mm; film thickness 0.25 μm). The injector and detector port (GC 14A) temperatures were set at 280 and 300 °C, respectively. The oven temperature was programmed to remain at 180 °C for 1 min and afterwards to increase from 180 to 280 °C using a 4 °C min^{-1}temperature gradient. In order to check the thermal stability of the model compounds, control experiments were performed using the same experimental conditions, but without light. Standard samples were eluted under the same conditions to allow comparative evaluations. The variation in the content of phenolic hydroxyl groups during the reaction was monitored using a spectrophotometric method proposed by Wexler [32].

The model-compounds were modelated using the semi-empirical method AM1 (Hyperchem 5.11). The charge distribution was employed in the discussion about the reactivity of these compounds.

3. Results and discussion

Fig. 2 shows a gas chromatogram of the degradation products of model compound (IV) after 4 h of irradiation in the

Table 1
Net charge on some atoms of the studied compounds, calculated after structure optimization (AM1)

Atom	Model			
	(I)	(II)	(III)	(IV)
1[a]	0.233	0.017	0.077	−0.080
2	−0.222	−0.190	−0.201	−0.186
3	0.044	0.020	0.044	0.067
4	−0.182	−0.188	−0.118	−0.183
5	0.062	0.064	0.046	0.053
6	−0.164	−0.184	−0.175	−0.172
7	−0.186	−0.209	−0.136	−0.105
8	−0.101	−0.078	−0.106	−0.129
9	0.079	0.073	0.072	0.080
10	−0.002	0.037	0.026	−0.001
11	−0.197	−0.193	−0.202	−0.199
12	0.038	0.033	0.034	0.040
13	0.066	0.055	0.053	0.063
14	−0.168	−0.167	−0.150	−0.169

[a] From substituent R_1 (see Fig. 5).

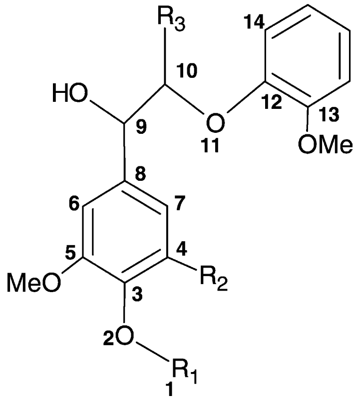


Fig. 5. General structure of the studied model compounds.

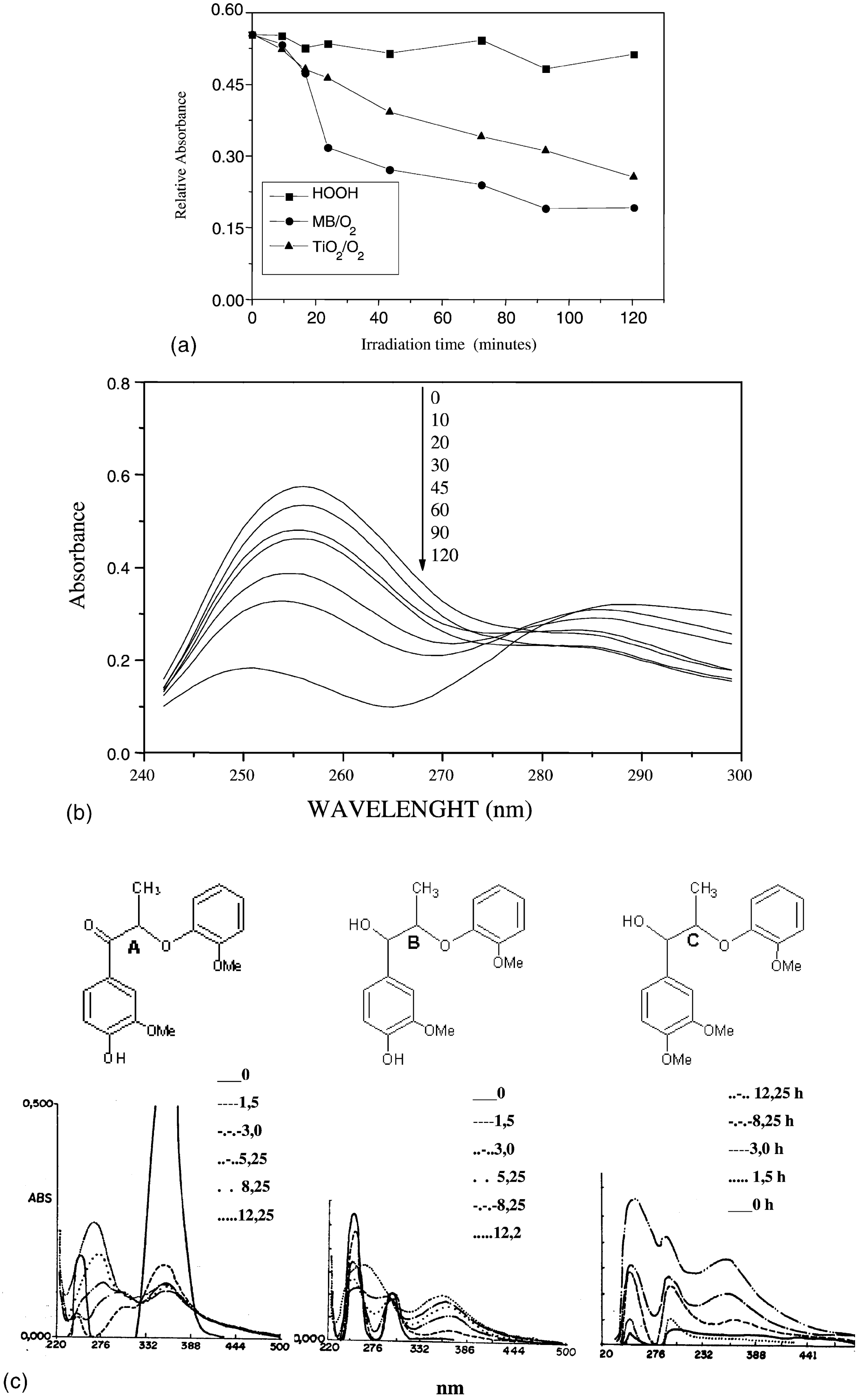


Fig. 6. (a) Relative changes in the content of phenolic OH during the degradation of model compound I under different reaction conditions. (b) Changes in the absorbance due to phenolate ion (255 nm), occurred during the photochemical degradation of model compound I, induced in the presence of hydrogen peroxide and alkaline medium. (c) Changes in the absorption band attributed to phenolate ion (255 nm), during the photodegradation of the lignin model compounds A, B, and C in methanolic solution as function of the irradiation time.

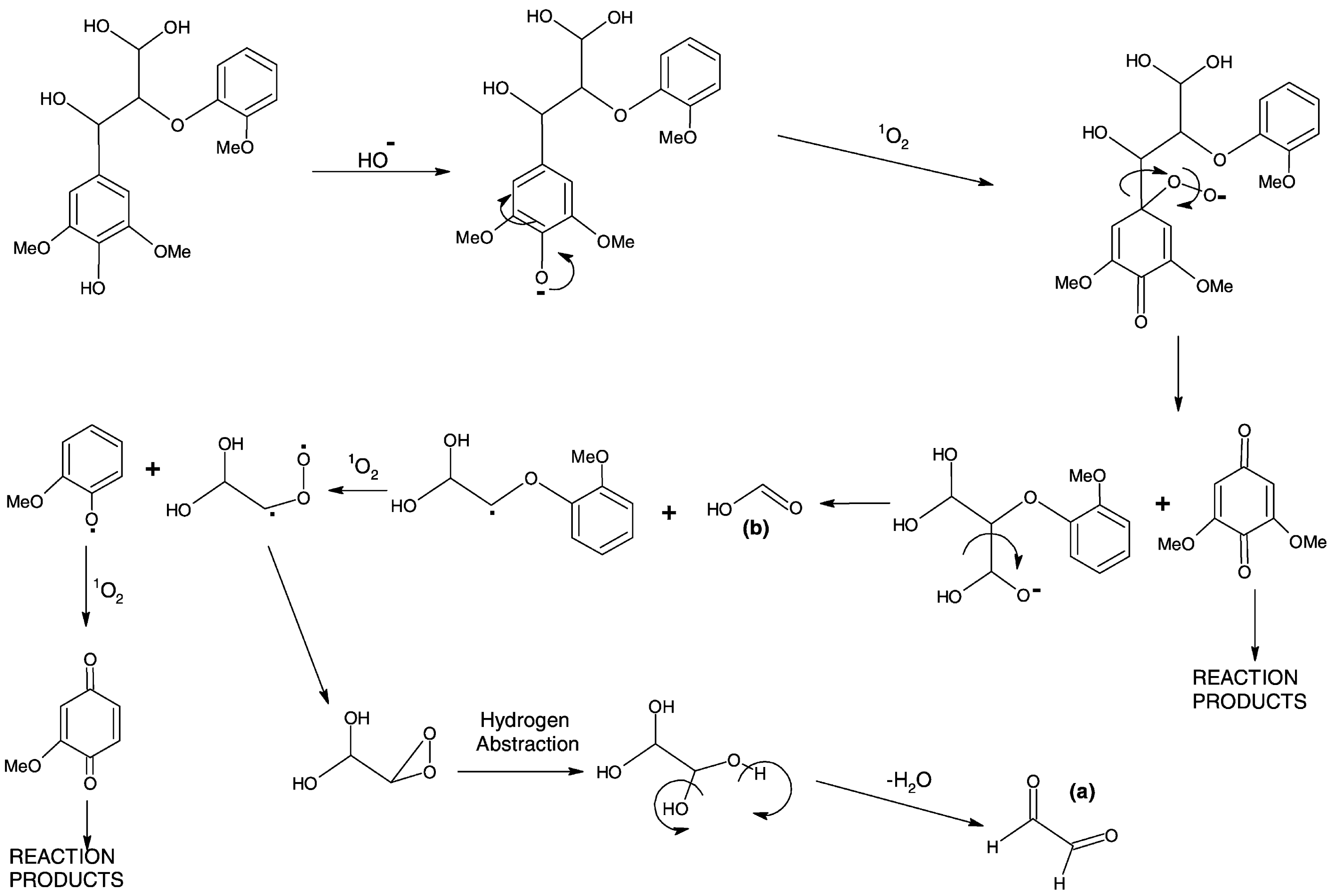


Fig. 7. Scheme for the degradation of model compound I mediated by singlet oxygen: (a) and (b) were not detected because they are eliminated during solvent evaporation.

presence of hydrogen peroxide at alkaline pH (pH ∼ 11). The first peak was identified as the starting compound, and the second as coniferyl alcohol.

Although, a complex mixture of products must be expected for the reaction mediated by hydrogen peroxide under alkaline pH, even in the absence of light [6,29]. One of the reactive species expected to be generated is the superoxide anion [33], which can be incorporated to the monomethoxylated ring, favoring the scission of the β-*O*-4 bond. On the other hand, the hydroxyl radical is the most reactive specie known. It is expected that during the reaction by the hydroxylation of the aromatic rings, be mediated by this species, principally on the phenoxyl ring, which is less protected. Even considering that the solvent can quench a great part of these radicals, the concentration of substrates in solution is sufficiently low and the amount of the added hydrogen peroxide is considerably high to justify that the models under study will be also efficiently attacked.

The expected result is the rupture of the β-*O*-4 bond, followed by the formation of coniferyl alcohol, and the opening of the phenoxy ring (Fig. 3).

Many products, however, were not detected most probably because, being volatile alkylic fragments, they were carried by the solvent during the evaporation procedure.

The next figure exemplifies the considerable complexity of the mass spectrum of the peak from gas chromatography, attributed to coniferyl alcohol. It was confirmed by comparison with the mass spectrum obtained for this compound. The fragments peaks at $m/z = 180$ (M^+), 151 (–CO) and 124 (M^- C_3H_4O) were taken as reference (Fig. 4).

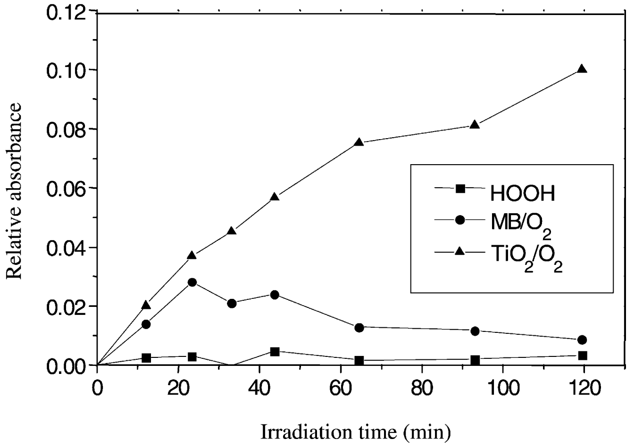


Fig. 8. Changes in the phenolic OH content during the degradation of the model compound II.

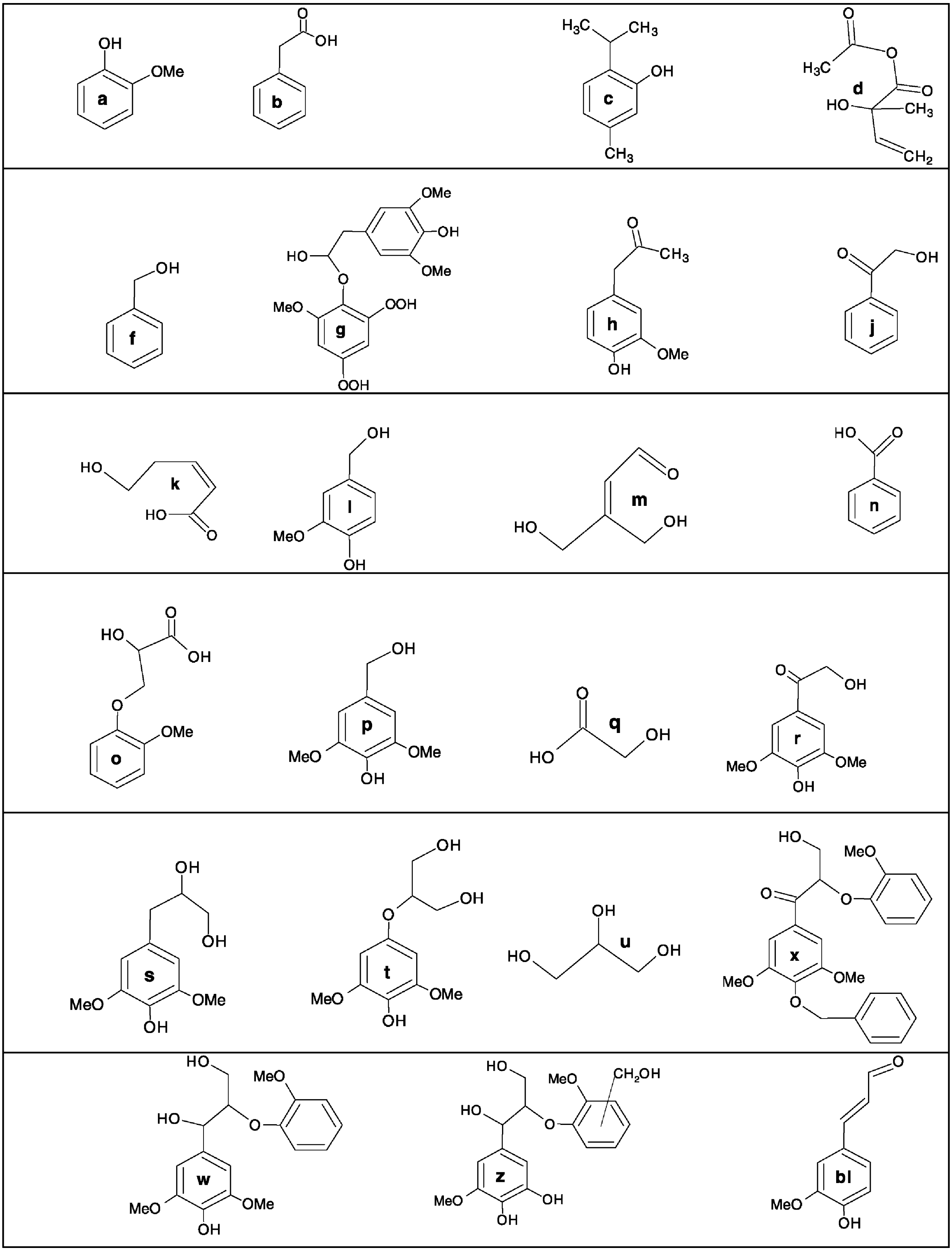


Fig. 9. Principal fragments identified between the degradation products.

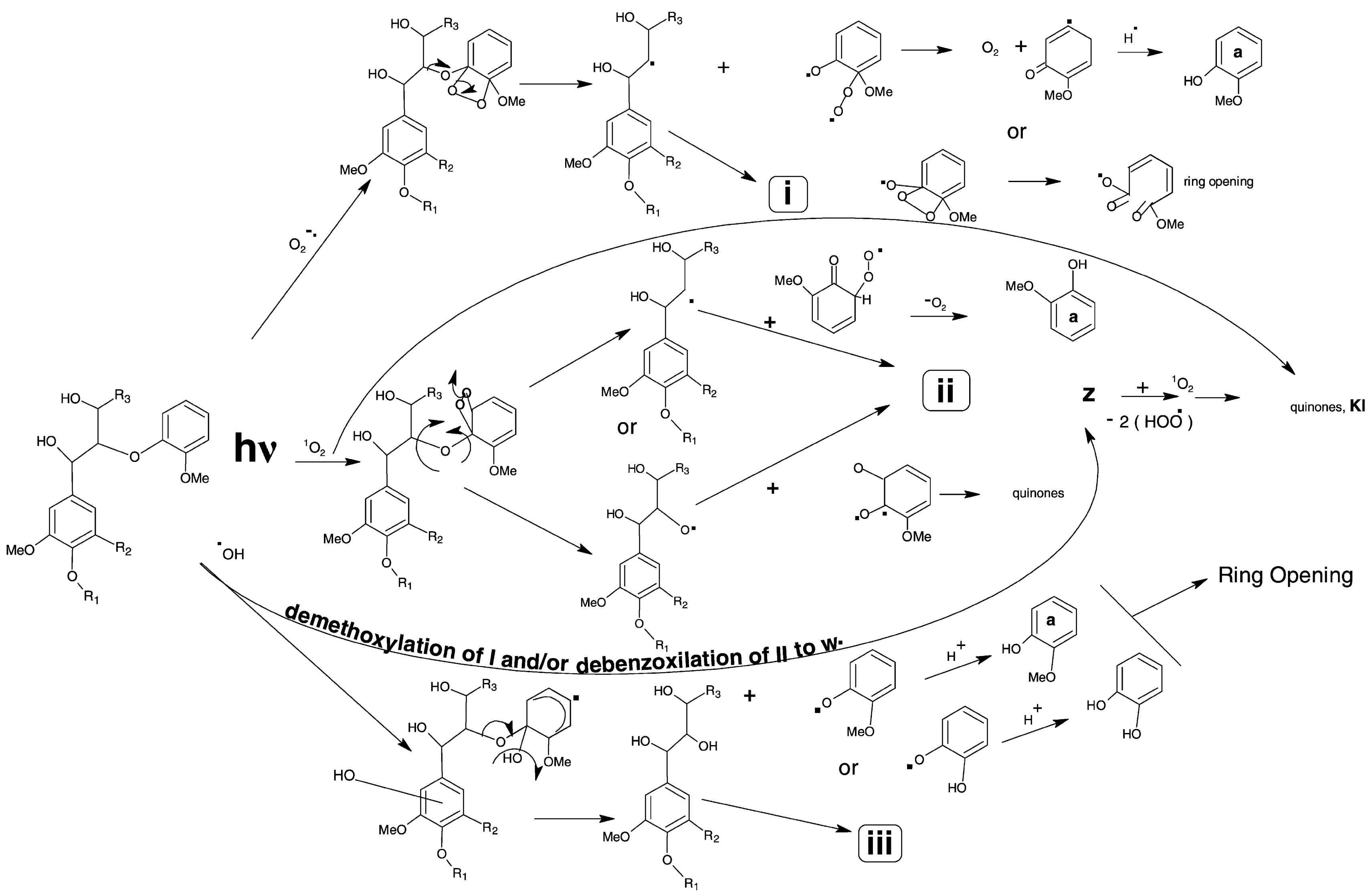


Fig. 10. General scheme for degradation of the studied model compounds.

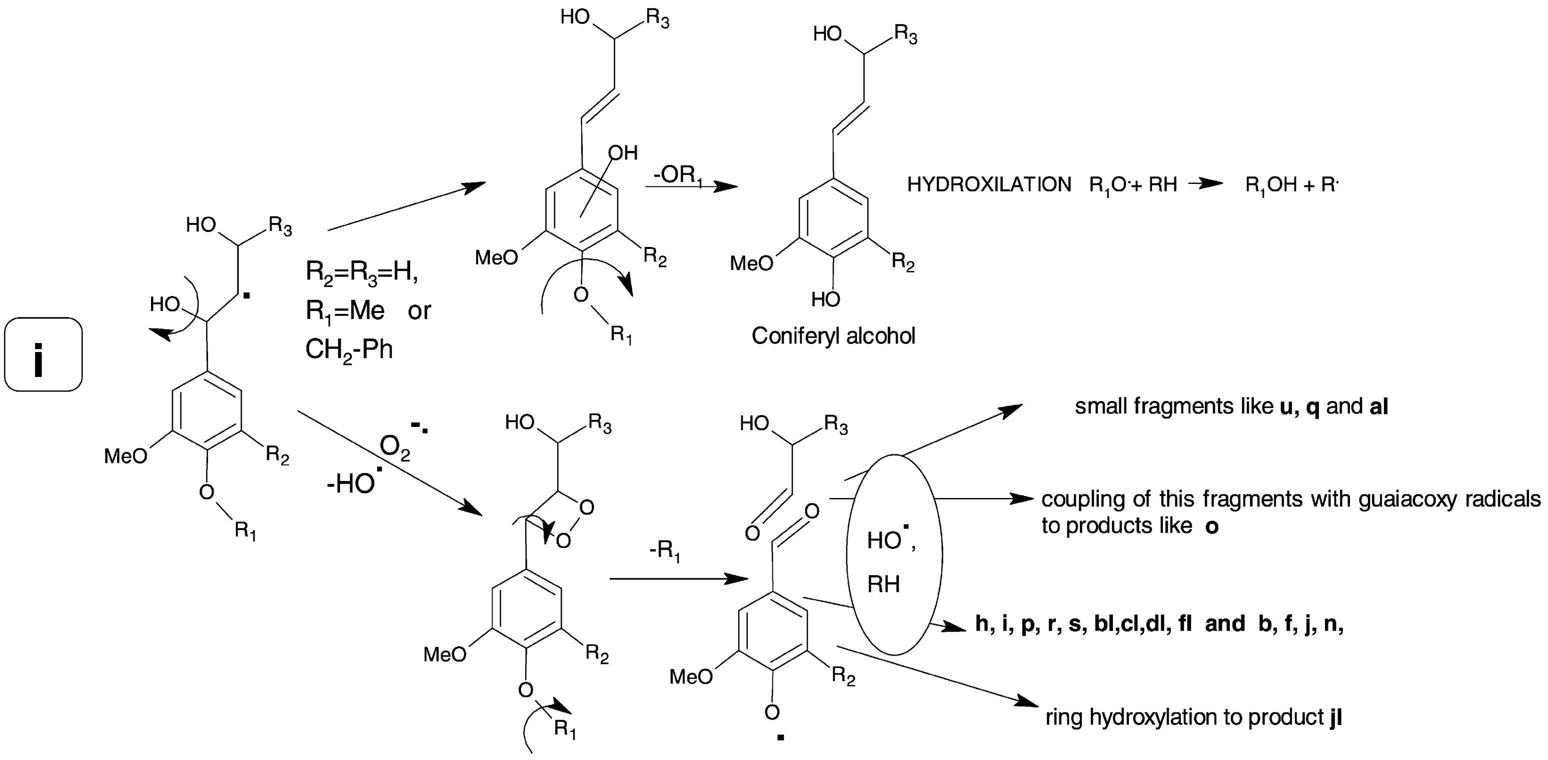


Fig. 11. Degradation of the phenacyl moiety in route (i).

To support our discussion, the electronic charge distribution over the atoms that constitute the compounds under study was estimated. The values obtained for the four models are in Table 1.

The charge distribution over the atoms of the compounds under study is approximately independent of the substituents R_1, R_2 and R_3. For the degradation of model (IV) mediated by hydroxyl radicals, as example, the most favorable positions to be attacked are 3, 5, 12 and 13 (Fig. 5). The same can be expected for the other model compounds.

The direct attack of the atom 9 by hydroxyl radicals is improbable, since that it is an alkylic carbon. On the other hand, the attack of the positions 12 and 13 by a superoxide anion, with the formation of an endoperoxide intermediate, can be expected in the reactions via photosensitization under alkaline pH, due to the electron deficiency of these atoms.

In a previous work, we have shown that the efficient cleavage of the β-*O*-4 bond depends on the position of the methoxyl substituent in the phenoxy ring [6]. As can be seen fromFig. 6a and 6b, for the degradation induced by the photochemical decomposition of hydrogen peroxide in alkaline medium, the relative rates of consumption of phenolic hydroxyl groups did not change appreciably.

This behavior could be due to the small concentration of $HO^\bullet$ relative to that generated by heterogeneous photocatalysis mediated by TiO_2, where the concentration is small but approximately constant due to the special character of the reaction. For the other two processes, an important reduction in the content of phenolic hydroxyl can be noted, which must be related to the destruction of aromatic rings. This reduction shows to be more evident when the process is mediated by photosensitization, where singlet oxygen and superoxide anion are the reactive species. Due to the alkaline pH of the reaction medium, hydroxyl radical must be also expected as reactive species in the photosensitized reaction.

These data are not conclusive when used as an isolated analysis. However, when we compare with other parameters and/or conjugated with other techniques, an important set of informations on the reaction can be obtained. For example, when no carbonyl groups are present in the model compound structure, phenolate bands occur only at about 250 and 300 nm (see model B at zero time of illumination in Fig. 6c). If carbonyl groups or conjugated π system are

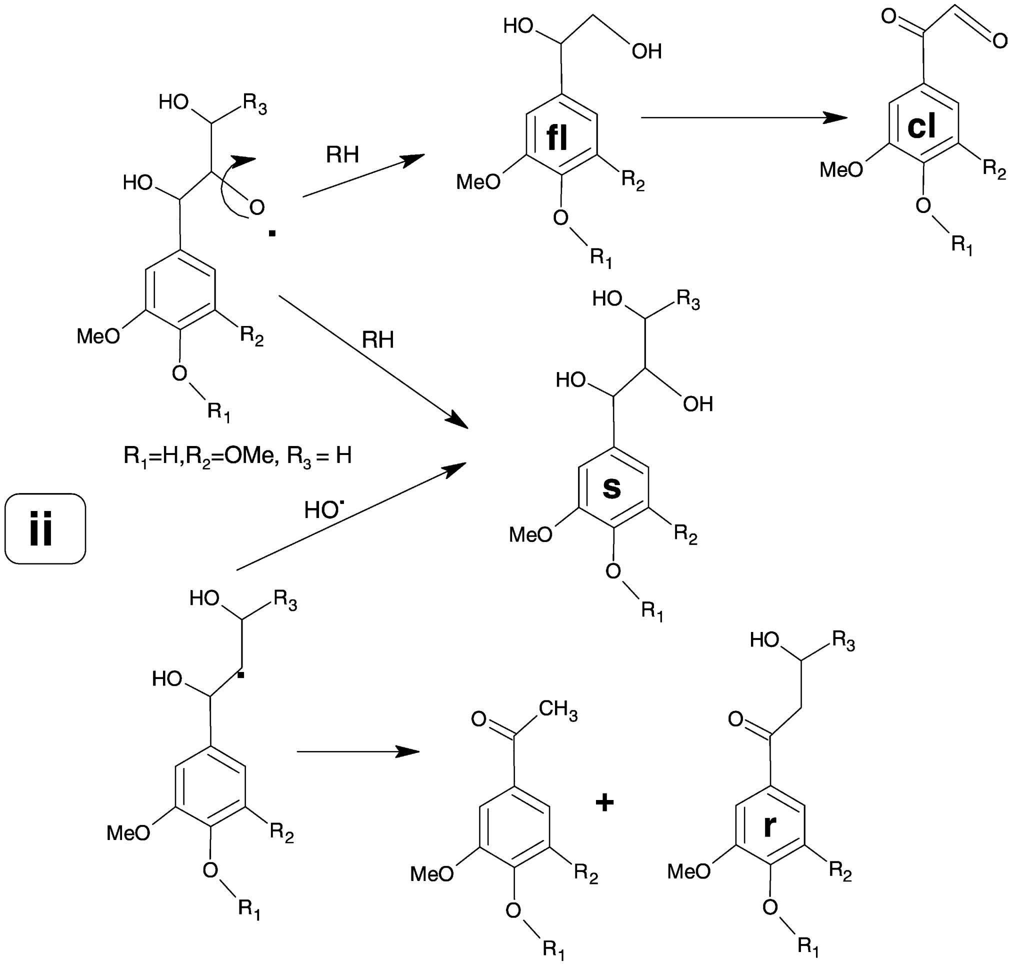


Fig. 12. Degradation of the phenacyl moiety in route (ii).

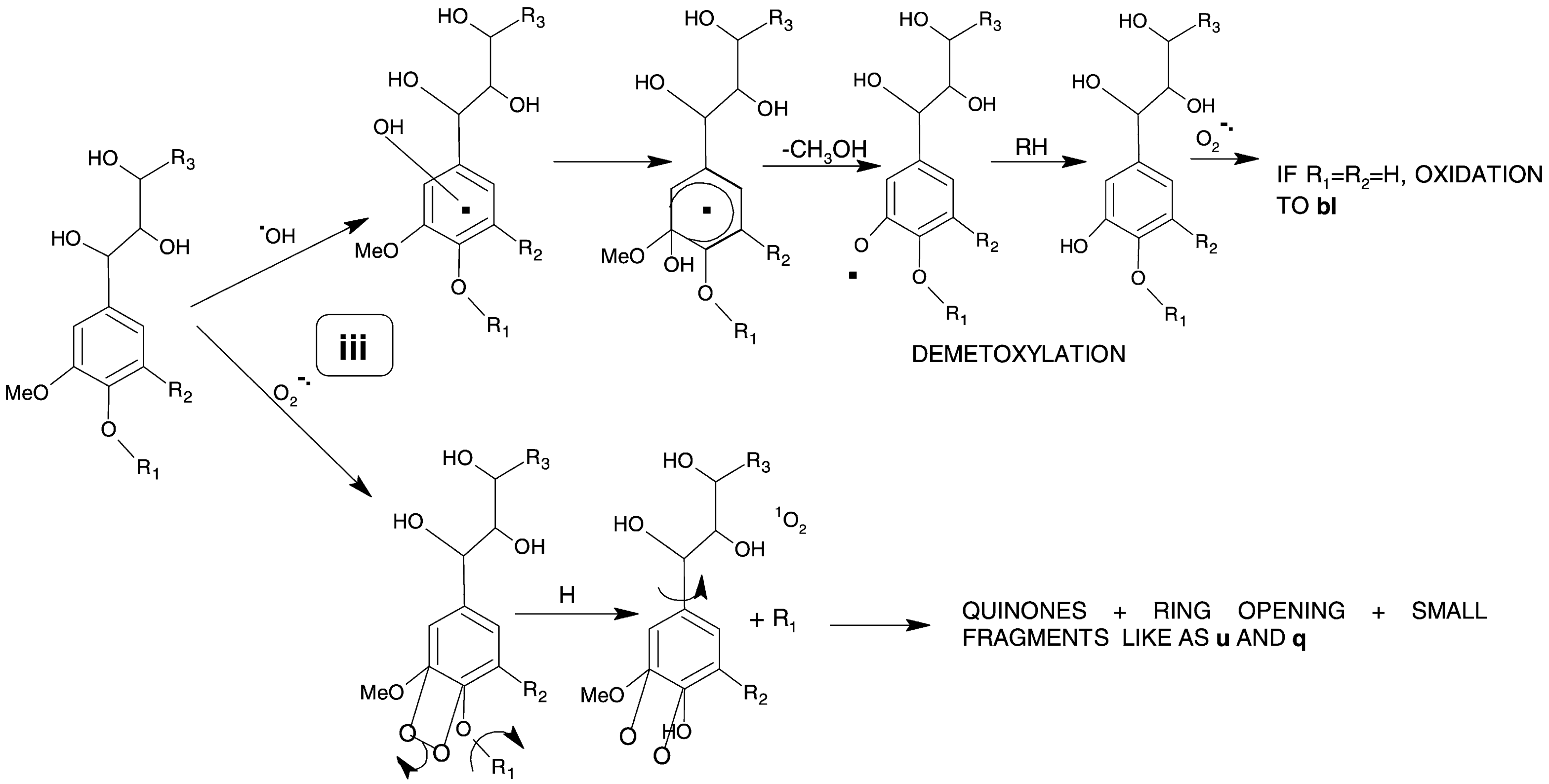


Fig. 13. Degradation of the phenacyl moiety in route (iii).

present at the α position of the phenyl propane unit, the band near 255 nm tends to disappear. On the other hand, if carbonyl groups are present at the α position, an increase in the absorbance band above 300 nm can be observed (around 350 nm). Previous results obtained by us, studying the degradation of β-*O*-4 models under both air and inert atmosphere (N_2), showed that for short photolysis times (below 120 min) the system does not suffer perceptible changes. For longer photolysis times, the evidences of oxidation increase significantly (Fig. 6c) [34].

In the mechanism mediated by photocatalysis an intense incorporation of hydroxyl radicals to the aromatic rings must be expected, with the ring opening occurring only after a significant period of irradiation [35]. On the other hand, considering the comparatively high complexity of the photosensitized reaction, the results furnished are better, as show Fig. 6a.

Some of the products of these reactions that were not lost with the solvent during concentration procedure are carbonylated compounds, as shown in the Figs. 4 and 6. They are responsible for the decrease in the absorbance at 255 nm with the concomitant increase of the band at 350 nm [36].

The lower degradation rate mediated by TiO_2, when compared with the photosensitized reaction, observed in Fig. 6a, can be attributed to an initial competition between incorporation of hydroxyl groups and degradation of the aromatic rings [19,20]. In the case of the photosensitized reaction, the reaction must be directed mainly by superoxide anion-radical and singlet oxygen, giving a more evident indication of degradation. In a simple manner, Fig. 7 exemplifies a part of the expected.

Although our previous results referred to the degradations mediated by photosensitization be in agreement with the work of Crestini and D'Auria [37,38], the actually proposed degradation mechanism differs, most probably due to the high pH in which the reactions were performed. Under the applied conditions, we expect that the action of superoxide anion be more evident than singlet oxygen.

It is premature to treat the trends shown in Figs. 6a, b and 7 as being associated to an efficient or not degradation, based on only one parameter such as the variation in the content of phenolic hydroxyl groups in the aromatic ring. Usually, the action of hydroxy radicals results in efficient processes related to the degradation of aromatics [19,38,39], lignin model compounds [40–42] and lignin and fragments [45]. In the processes in which hydroxy radicals are generated, like the reactions (a) and (c) discussed in this work, the complete mineralization of the model compounds will occur after long times of reaction, principally if, as occur in the photocatalytical processes, the amount of radicals be autosustainable [24,25]. The results furnished by the photocatalytical process, when compared with the given by the process based on the photochemical decomposition of hydrogen peroxide, can be considered advantageous, since that the amount of hydroxy radicals produced reach during the initial steps of the reaction an approximately constant concentration (a stationary concentration) which is maintained during all process. The physical and morphological characteristics of the catalyst are fundamental to promote efficiently the reactions [43,44]. For some lignin fragments, as example, anatase has been proposed as an efficient catalyst [44]. In other situation, a mixture anatase/rutile (P25, Degussa) showed to be the best catalyst [45]. Obviously, a detailed investigation of the occurred after a given reaction time is a pre-condition to define which process is the most efficient.

Table 2
The fragments observed by GC–MS

System/model compound	a (H_2O_2)	b (MB/O_2)	c (TiO_2/O_2)
I	a, q, r, s, u	a, w, bl	a, n, r, s, w, kl
II	a, n, o, p, q, r, s, t, u	a, w	a, n, p, r, s, u, w, x, y, z
III	a, b, c, d	a, f, g	a, h, j, k, l, m

Our previous results involving the bleaching of cellulosic pulps show that the photocatalysis gives best results compared to the photosensitized one, principally if the aim is to preserve the integrity of the cellulosic pulp [23]. The process mediated by hydrogen peroxide and UV light presents an intermediate efficiency.

The behavior observed during the degradation of the model II, promoted by TiO_2 (Fig. 8), can be explained considering that the structure fragmentation jointly with the incorporation of hydroxy radicals by the aromatic structures results in more phenolic hydroxyl groups. The photosensitized reaction follows initially an equivalent behavior, but probably only due to the structural fragmentation, since that in this process hydroxy radicals are not generated. The similarity between the two processes stops after 20 min of reaction when probably the oxidation of the aromatic structures is initiated.

The behavior presented by the reaction induced by the active species produced from the decomposition of hydrogen peroxide by UV light, leads us to conclude that under these conditions is occurring a very small incorporation of hydroxy radicals by the aromatic rings, as occurs for the model compound I under the same conditions. This can be taken, as an indication that the reaction promoted by this kind of degradation is very different from the proposed to occur by photocatalysis, but it cannot be considered as an indication that this degradative process is inefficient. By the analysis of the fragments obtained in the three processes is concluded that the processes (a) and (c) are the most aggressive for the models compounds under investigation. Table 2 and Fig. 9 show the principal fragments obtained for the three processes.

From Table 2 and Fig. 9, species derived from ring opening can be systematically identified from the application of processes (a) and (c).

A summary of our conclusions is presented in the general scheme (Fig. 10), detailed in Figs. 11–13.

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