

Photoreactivity of lignin model compounds in the photobleaching of chemical pulps

1. Irradiation of 1-(3,4-dimethoxyphenyl)-2-(3'-methoxyphenoxy)-1,3-dihydroxypropane in the presence of singlet oxygen sensitizer or hydrogen peroxide in basic methanol solution

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Abstract

The irradiation of 1-(veratryl)-2-(3'-methoxyphenoxy)glycerol in alkaline methanol solution was performed in the presence of hydrogen peroxide (UV and visible light) and sensitized by methylene blue (MB) in the presence of O₂ (visible light). The photoproducts were analysed by gas chromatography–mass spectrometry (GC–MS). The β-O-4 ether bond cleavage, which usually occurs in reactions involving singlet oxygen, was not operative, since the corresponding phenol **3** was detected in trace amounts only and the carbonyl derivative **4** was not detected at all. Irradiation in the presence of MB/O₂ induced the oxidation of the benzyl group into a carbonyl function and produced the hydroxymethylation of one benzene ring of compound **1**. In contrast, such reactivity was not observed when **1** was irradiated in the presence of H₂O₂; nevertheless, hydroxylation of one benzene ring was detected. For both types of irradiation, four stereoisomers were formed. The mass spectrum showed the addition of hydrogen peroxide to the B benzene ring of compound **1**. This is the most important reaction, and was ascribed to the radical addition of a superoxide anion assisted by the hydroxyl groups in the β or γ positions of the glycerol moiety. © 1997 Elsevier Science S.A.

Keywords: Hydrogen peroxide; Lignin; Lignin model; Photobleaching; Photolysis; Singlet oxygen

1. Introduction

The importance of minimizing the use of chlorine derivatives in wood bleaching has increased in recent years because of stricter pollution regulations. Bleaching with oxygen-containing reagents has received great attention and is now applied on a large scale. Of these reagents, hydrogen peroxide has been used to bleach high-yield and chemical pulps. The generally accepted mechanism of bleaching involves perhydroxyl ions in the presence of alkali [1,2], the brightening effect being due to the reaction of various coloured carbonyl structures present in lignin, including quinones and substituted cinnamaldehyde. Hydroxyl radicals and other oxygen radical species, generated by hydrogen peroxide decomposition, are responsible for the delignification process [3–6]. The potential benefit of using bleaching species in conjunc-

tion with UV light has been recognized for chlorine [7], chlorine dioxide [8], oxygen [9,10] and hydrogen peroxide [11–14].

It has been shown by Machado et al. [15,16] that hydrogen peroxide in alkaline medium and UV light promote strong delignification of various soluble lignin and lignin model compounds. Quenching experiments have confirmed the involvement of singlet oxygen, produced by the decomposition of hydrogen peroxide at alkaline pH, as the main cause of the rapid breakdown of the lignin polymer [15,16]. Recently, we have found [13] that efficient delignification of *Eucalyptus grandis* organosolv pulp can be achieved using three photochemical stages in alkaline medium (NaOH) at 85 °C. The first stage involves oxygen treatment, followed by a reaction sensitized by methylene blue (MB) in the second stage. The last stage, using hydrogen peroxide, is the most efficient, the structure of the lignin polymer being prepared by the first two stages. Nevertheless, the mechanism of

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the overall process remains unknown. This work contributes to the knowledge of the photodelignification process. We investigate the photochemical action of hydrogen peroxide and a singlet oxygen sensitizer (MB) on a lignin model molecule, 1-(3,4-dimethoxyphenyl)-2-(3'-methoxyphenoxy)-1,3-dihydroxypropane **1**, in basic methanol solution. The meta position of the methoxyl group in the phenoxy moiety was chosen to increase the photochemical effect of the substituent [17].

2. Experimental details

2.1. General

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 250 FT spectrometer (reference Me_4Si , solvent CDCl_3). IR absorption spectra were obtained on a Perkin-Elmer Paragon 1000 PC spectrometer. Mass spectra were obtained using a VG Micromass using electron ionization (EI, 70 eV) or chemical ionization (CI, NH_3) modes. The purity of the synthesized compounds was confirmed by gas chromatography (GC) and their structures were obtained by IR, ^1H NMR and mass spectrometry. The majority of the chemicals used in this study were purchased from Aldrich, and were used as received.

2.2. Photolysis of compound 1

A $1.5 \times 10^{-3} \text{ mol l}^{-1}$ solution of the substrate in methanol (10 ml), made alkaline with 0.025 ml of aqueous 2 M NaOH solution, was irradiated for 4 h in the presence of either H_2O_2 (0.6 ml of a 30% solution; final concentration, $5 \times 10^{-2} \text{ mol l}^{-1}$) or MB (0.05 ml of a $4.5 \times 10^{-3} \text{ mol l}^{-1}$ aqueous solution; final concentration, $2.25 \times 10^{-3} \text{ mol l}^{-1}$) with oxygen bubbling. The irradiation set-up consisted of two parallel medium-pressure mercury lamps (400 W), surrounded by a Pyrex glass jacket for water circulation, and a fan directed towards the sample to maintain the temperature at 25 °C. The distance of each lamp from the sample was 5 cm. For the MB experiments, a solution of sodium nitrite (80 g l^{-1}) was placed around the reaction flask in order to cut out UV light.

After photolysis, the solvent was evaporated under vacuum at 25 °C to 0.5 ml and acidified to pH 1–2 with HCl. The organic compounds were extracted with CH_2Cl_2 (2 ml). The organic phase was transferred to a conical flask, and the solvent was evaporated to dryness under vacuum. The solid dry photoproducts were dissolved in 100 μl of dry tetrahydrofuran (THF) and silylated with bis(trimethylsilyl)trifluoroacetamide (50 μl) in the presence of pyridine (20 μl). The same procedure was performed for the reference compounds **2** and **3**. The analyses of the photoproducts were performed by GC with a flame ionization detector (Shimadzu GC 14A equipped with a C-R4A chromatopac data analyser) or gas chromatography-mass spectrometry (GC-MS) (Hewlett Packard 5890 chromatograph interfaced with the

mass spectrometer) on a capillary column (J and W Scientific) ($30 \text{ m} \times 0.25 \text{ mm}$; film thickness, 0.25 μm ; stationary phase DB-5MS). The injector and detector port (GC14A) temperatures were set at 280 and 300 °C respectively. The oven temperature programme was 180 °C (1 min) and between 180 and 300 °C with a gradient of 4 °C min^{-1} . Control experiments were performed with the same experimental conditions, but without light, in order to check the thermal stability of compound **1**.

2.3. Syntheses

2.3.1. Compound 2

Condensation of 3-methoxyphenol (30 mmol) with α -bromoacetoveratone [18] (24 mmol) in the presence of potassium carbonate (40 mmol) and sodium iodide (3 mmol) in acetonitrile at reflux temperature for 12 h yielded α -(3-methoxyphenoxy)acetoveratone after usual work-up and chromatography on silica gel (eluent, dichloromethane). Yield, 75%. The hydroxymethylation of the carbonyl derivative was performed by reacting the compound (18 mmol) with 35% HCHO (25 mmol) in a mixture of ethanol (70 ml) and acetone (70 ml) in the presence of potassium carbonate (5 mmol) at 30 °C for 12 h. Evaporation of the solvent, extraction of the solid residue with dichloromethane and chromatography on silica gel (eluent, dichloromethane-diethyl ether (3 : 2 v/v)) allowed the isolation of compound **2** as a white solid. Yield, 50%; m.p., 136 °C.

^1H NMR (CDCl_3) δ ppm: 2.85 (t, OH, 1H), 3.68 (s, OCH_3 , 3H), 3.80 (s, OCH_3 , 3H), 3.90 (s, OCH_3 , 3H), 4.05 (m, CHCH_2OH , 2H), 5.50 (t, CHCH_2OH , 1H), 6.3–7.8 (m, ArH, 7H). IR (KBr) ν : 3500, 2940, 1690, 1590, 1510, 1270, 1150, 1090 and 860 cm^{-1} . MS of the trimethylsilyl derivative: 404 (M^+ , 10%), 281 (3%), 254 (21%), 165 (100%), 150 (13%), 73 (16%).

2.3.2. Compound 1

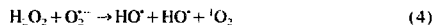
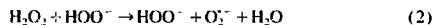
Reduction of compound **2** (4.5 mmol) was performed with NaBH_4 (26 mmol) in ethanol (100 ml) at 50 °C for 8 h. After evaporation of the solvent, the residue was treated with dilute HCl and extracted with diethyl ether. The organic phase was dried with sodium sulphate, evaporated and the resulting mixture was chromatographed on silica gel (eluent, CH_2Cl_2 - Et_2O -MeOH (72 : 25 : 3, v/v/v)) giving compound **1** as a white solid. Yield, 85%. GC of the silylated compound indicates the presence of two diastereoisomers (34% erythro and 66% threo). The assignment was based on ^1H NMR studies performed by Brunow et al. [19] on similar structures which indicate the predominance of the threo form when the carbonyl derivative is reduced with sodium borohydride.

^1H NMR (CDCl_3) δ ppm: 3.6–3.8 (m, OCH_3 + H_γ , 10H), 4.25 (m, H_γ , 1H), 4.9 (m, H_β , 1H), 6.25–7.1 (m, ArH + H_α , 8H). IR (KBr) ν : 3450, 3380, 2940, 1605, 1515, 1260, 1150, 1030 and 760 cm^{-1} . MS of the trimethylsilyl derivative: 478 (M^+ , 3%), 239 (100%), 73 (32%).

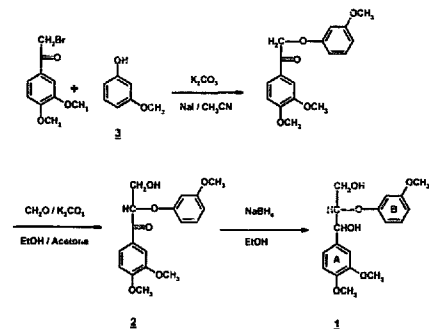
3. Results and discussion

Compound **1** was prepared with an overall yield of 32% starting from α -bromoacetoveratrone using the synthetic procedure outlined in Scheme 1. A similar reaction scheme was used for the preparation of guaiacylglycerol- β -guaiacyl or syringyl ethers [20].

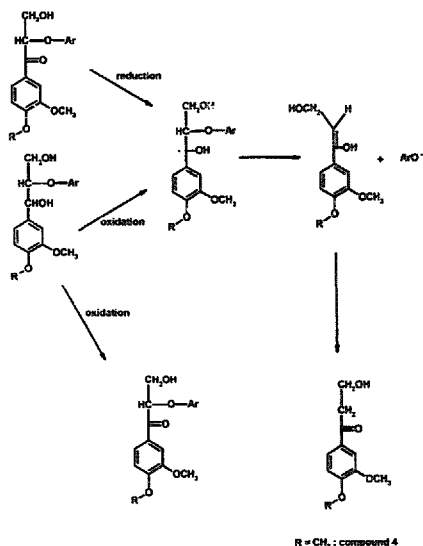
The β -O-4 ether linkages represent about 50% of the structural units of the lignin polymer. Their cleavage is a very important step in the delignification process to obtain fully bleached chemical pulp. Photochemical studies on the mechanism of brightness reversion of bleached mechanical pulps have shown the importance of the ketyl radical generated either by photoreduction of the α -carbonyl β -O-4 units [21,22] or by oxidation of the benzylic alcohol group in the guaiacyl or syringyl glycerol- β -aryloxy structural elements [23]. Moreover, the oxidation of the benzylic alcohol into a conjugated carbonyl group was shown to be competitive with the ketyl radical reaction [24]. These oxidation pathways are described in Scheme 2. Hydrogen peroxide in alkaline medium on UV light exposure generates various active oxygen species [16] able to react with the lignin structural elements



To check these photoreactive pathways, compound **1** was irradiated for 4 h in methanol solution ($1.5 \times 10^{-3} \text{ mol l}^{-1}$) in the presence of sodium hydroxide to maintain the medium



Scheme 1. Synthesis of compound **1**.

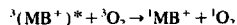


Scheme 2. β -O-4 ether bond cleavage of the ketyl radical according to Refs. [21,22] and photo-oxidation of the benzylic alcohol moiety into a carbonyl structure [24].

alkaline. In one set of experiments, the solutions were irradiated in the presence of H_2O_2 ($5 \times 10^{-2} \text{ mol l}^{-1}$) with light emitted from medium-pressure mercury lamps, which give emission in both the UV (above 300 nm) and visible. With these conditions, hydroperoxyl (HOO^\bullet) and hydroxyl (HO^\bullet) radicals, singlet oxygen (${}^1\text{O}_2$) and superoxide anion (O_2^-) are the reactive species formed. Due to the alkaline nature of the reaction medium, it is expected that superoxide anions and hydroxyl radicals will be the principal reactive species as a result of deactivation of singlet oxygen [25] according to



In another set of experiments, MB ($2.25 \times 10^{-3} \text{ mol l}^{-1}$) and oxygen bubbling were used, the UV part of the mercury lamp emission being eliminated with an NaNO_2 filter. In these conditions, singlet oxygen and superoxide anion can be produced. Usually, in non-alkaline medium, the generation of singlet oxygen is photosensitized by MB with a good quantum efficiency (0.50) in methanol [26]



In addition, due to the quenching of singlet oxygen by hydroxyl ions, superoxide ions and hydroxyl radicals are expected to be reactive species. In the absence of MB, no

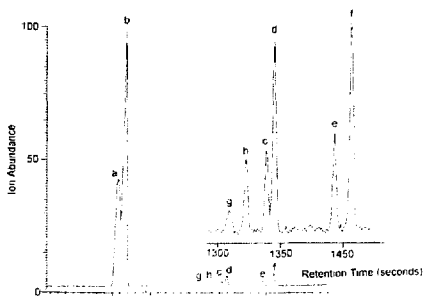


Fig. 1. Gas chromatogram of the complex mixture of products obtained after irradiation of compound 1 for 4 h in alkaline methanol in the presence of H_2O_2 . The short retention period related to the solvent and silylation reagents was omitted for clarity.

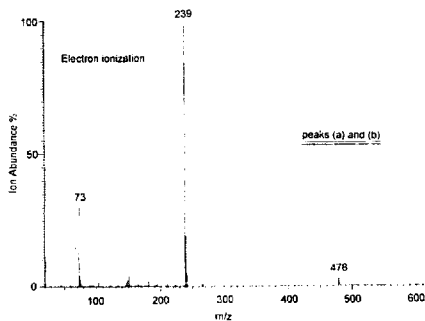


Fig. 3. Mass spectrum related to peaks (a) and (b).

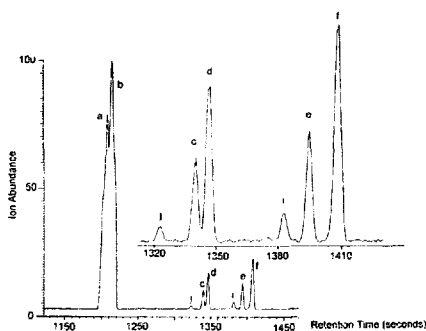
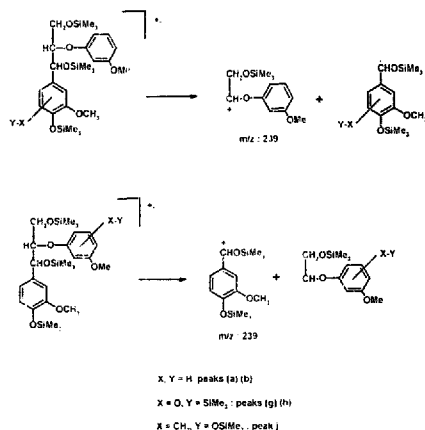


Fig. 2. Gas chromatogram of the complex mixture of products obtained after irradiation of compound 1 for 4 h in alkaline methanol in the presence of MB and oxygen bubbling.

reaction occurs. The conversion rates are around 5% for H_2O_2 and 20% for MB.

The complex mixture of products obtained after irradiation was analysed as trimethylsilyl derivatives using GC coupled with MS. The chromatograms display eight distinct peaks for irradiation in the presence of H_2O_2 (Fig. 1) and MB (Fig. 2) with (a), (b), (c), (d), (e) and (f) being identical signals. In the figures, the short retention periods, attributed to the response of the solvent and the silylating reagents, are not represented. Nevertheless, it is noteworthy that silylated 3-methoxyphenol is detected as traces at a retention time equal to 150 s for both irradiations and no evidence is obtained for the presence of the silylated carbonyl compound 4.

Peaks (a) and (b) correspond to the starting compound 1, (a) being attributed to the erythro stereoisomer and (b) to the threo stereoisomer (see Section 2). The mass spectrum obtained for the (a) and (b) peaks (Fig. 3) indicates that, under electron ionization, benzyl cleavage, giving ions $m/z=239$, is the major process (Scheme 3).



Scheme 3. Fragmentation pattern related to the mass spectrum of peaks (a), (b), (g), (h) and (j).

Oxidation of the benzyl alcohol into a carbonyl derivative is observed only for irradiation in the presence of MB. This may be attributed to electron transfer oxidation (type I photo-oxidation) induced by MB in the presence of oxygen [27]. Peak (i) is attributed to compound 2' according to its retention time and mass spectrum (Fig. 4) in comparison with those of an authentic sample. The main fragmentation process is the cleavage of the bond α to the carbonyl function ($m/z=165$); the peak at $m/z=254$ is probably due to the silylated veratric acid ion. The carbonyl derivative 2, despite its high photochemical reactivity, survives during photolysis because UV light is eliminated by the $NaNO_2$ filter.

Recently, Crestini and D'Auria [28] have reported, for the phenoxycetophenone derivatives, a high conversion rate (70%–80%) for a reaction induced by singlet oxygen generated by photosensitization. They demonstrated the

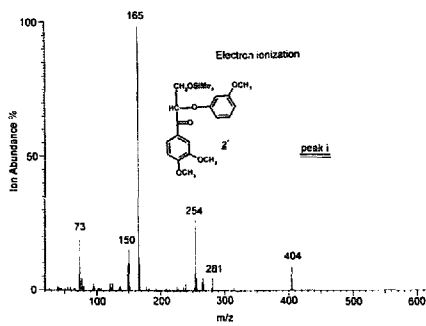


Fig. 4. Mass spectrum related to peak (i).

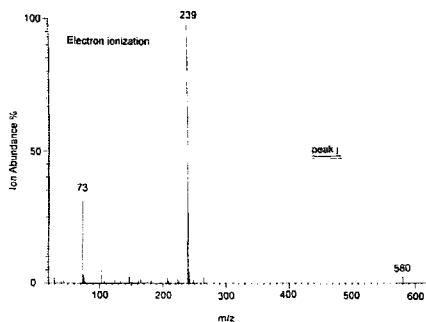
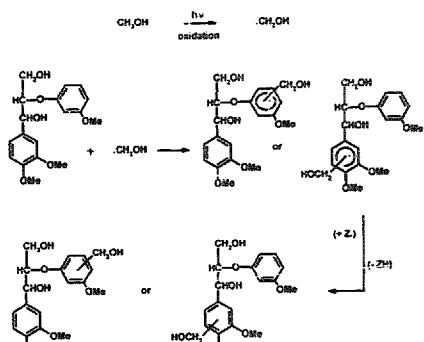


Fig. 5. Mass spectrum related to peak (j).

occurrence of β -O-4 bond cleavage in the reaction. The absence of β -O-4 bond cleavage during the photolysis of compound **1** in the presence of MB/O₂ supports the absence of reactive singlet oxygen in the medium. In addition, a compound given by peak (j) is only obtained during irradiation in the presence of MB. Its mass spectrum (Fig. 5) indicates the incorporation of the CH₂OSiMe₃ fragment in benzene ring A or B of compound **1** (Scheme 3). The compound may be formed by the addition of the \cdot CH₂OH radical, generated by the oxidation of methanol, on one benzene ring of compound **1**, followed by re-aromatization of the ring (Scheme 4).

Peaks (g) and (h), which are associated with the same mass spectrum (Fig. 6), are only observed when irradiation is conducted in the presence of hydrogen peroxide. The molecular ion shows that the hydroxylation of one of the benzene rings of compound **1** has occurred (Scheme 5). This is characteristic of the reaction of hydroxyl radicals with aromatic rings in lignin model derivatives [29] (Scheme 5). The hydroxyl radicals are produced by homolytic cleavage of hydrogen peroxide.

For both irradiations, a set of peaks (c), (d), (e) and (f) is observed. They display the same mass spectrum under



Scheme 4. Hydroxymethylation mechanism leading to the compound giving peak (j).

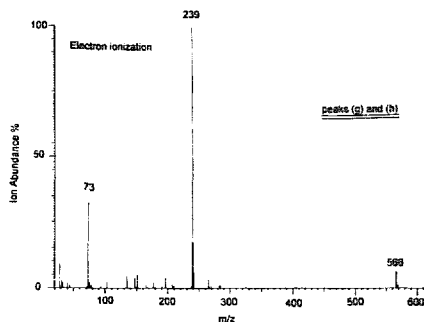
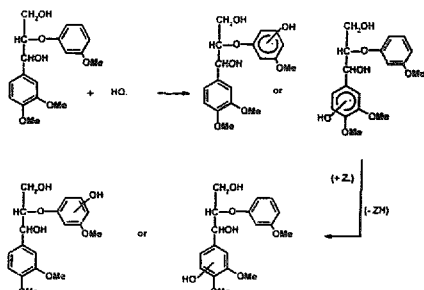


Fig. 6. Mass spectrum related to peaks (g) and (h).



Scheme 5. Hydroxylation mechanism leading to the isomers giving peaks (g) and (h).

electron and chemical ionization modes (Figs. 7 and 8). The molecular ion fragment indicates the addition of hydrogen peroxide to compound **1**. A fragmentation pattern is proposed

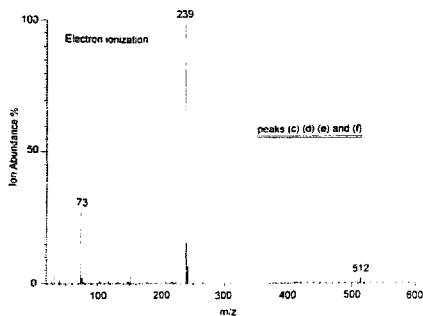


Fig. 7. Mass spectrum related to peaks (c), (d), (e), (f) and (h), electron ionization.

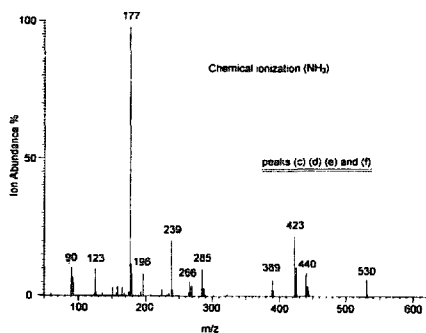
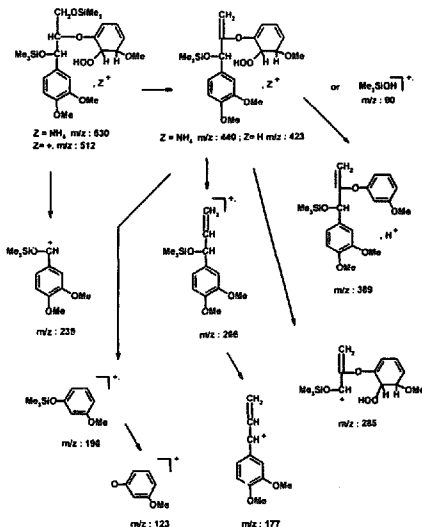


Fig. 8. Mass spectrum related to peaks (c), (d), (e), (f) and (h), chemical ionization.

in Scheme 6 for such addition on ring B. The OOH substituent is localized at the 2' position as this may explain why the hydroperoxide is not silylated due to steric hindrance. The existence of four peaks is associated with erythro–threo and cis–trans stereoisomerism. Nevertheless, the addition of HOOH on another part of the B ring cannot be excluded. These hydroperoxides may result from the action of superoxide anion, produced during the deactivation of singlet oxygen generated in the first step of both reactions, followed by radical addition on the 2' vertices. The formation of the hydroperoxides appears to be the principal reaction. The reactivity of this position may be enhanced by the presence of the OH group linking the negative oxygen of the peroxide group.

The electrophilic character of singlet oxygen does not appear to play a major role in the photochemistry of compound 1, otherwise dioxetane would be formed and different products would result, such as muconic aldehyde and esters. This agrees with its efficient deactivation promoted by hydroxyl ions.

Studies are presently being performed to assess the role of the methoxy substituent of the B ring on the photochemistry



Scheme 6. Fragmentation pattern related to the mass spectrum of peaks (c), (d), (e) and (f).

of the β -O-4 glycerol structures irradiated, or not, in basic medium in the presence of hydrogen peroxide or singlet oxygen sensitizer. The roles of singlet oxygen and superoxide anion remain unclear and need to be determined in order to develop a very efficient photobleaching process of chemical pulps.

4. Conclusions

The photoreactivity of veratrylglycerol- β -(3-methoxyphenoxy) ether in alkaline methanol has been investigated on exposure to UV–visible irradiation ($\lambda > 300$ nm) and in the presence of MB as singlet oxygen sensitizer ($\lambda > 400$ nm). An analysis of the photoproducts indicates that the oxidation of the benzylic alcohol moiety into a carbonyl derivative and the cleavage of the β -O-4 bond are minor processes. The structures of the photoproducts indicate that hydroxyl radical and superoxide anion are the main active oxygen species in the photochemical process. This conclusion must be extended and confirmed in the photobleaching of chemical pulps.

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