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Photodegradation of lignin: the role of singlet oxygen

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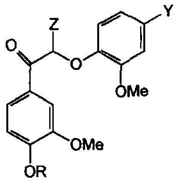
Abstract

The photochemical irradiation of some phenoxyacetophenone derivatives in the presence of oxygen by using visible light did not produce any decomposition product. In the presence of singlet oxygen, sensitized by using Bengal Rose, decomposition products were obtained. The products obtained were similar to those obtained by direct β-C–O cleavage on the substrate. In this case, the observed behavior can be explained assuming an attack of singlet oxygen on a phenoxy part of the molecule.

Keywords: Photodegradation; Lignin; Singlet oxygen; Visible light; Bengal Rose

1. Introduction

Some years ago, discussing a photochemical oxidation of lignin and using a model compounds styryl derivatives, Gellerstedt and Petterson [1] reported the involvement of singlet oxygen in the process via the formation of the corresponding endoperoxide which then led to products deriving from a carbon–carbon bond cleavage. Successively, using model compounds such as **1**, the irradiation of these compounds at both 300 and 350 nm in the presence of oxygen led to the cleavage products **2–5** in the presence of some amounts of phenolic products deriving from the oxidation of an aromatic ring [2–4].



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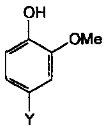

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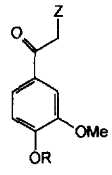

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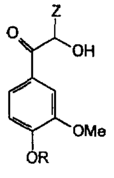

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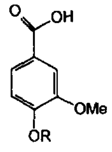

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The formation of cleavage products was explained by assuming that a β-C–O bond cleavage occurred in the first excited singlet or triplet state of **1** to give the phenacyl radical. The interaction of this intermediate with oxygen gave the products. While β-C–O cleavage was considered to be a primary photochemical step, singlet oxygen was involved in the oxidation of phenolic functions [5–7].

On the basis of these reported data, singlet oxygen may have some role in the photodegradation of lignin and, in particular, in the photo-oxidation of phenols, while spontaneous β-C–O seems to play the most important role in the fragmentation of the molecules. On the contrary, in this paper we wish to point out that singlet oxygen can play a fundamental role in the photodegradation of lignin models.

2. Experimental details

^{1}H nuclear magnetic resonance (NMR) spectra were recorded with a Bruker 300 AM instrument. Mass spectroscopy (MS) was performed with Hewlett–Packard 5971 mass-selective detector on a Hewlett–Packard 5890 gas chromatograph. Gas chromatography (GC) analyses were obtained using an OV-1 capillary column between 70 and 250 °C (20 °C min^{-1}).

2.1. 4-Ethoxy-3-methoxyacetophenone (7)

To a solution of acetovanillone (**6**) (4.15 g, 25 mmol) in dimethyl formamide (DMF) (40 ml), K_2CO_3 (1.15 equiv-

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alents, 4 g) and ethyl iodide (1.5 equivalents, 5.85 g) were added at 25 °C under magnetic stirring. After 2 h the reaction mixture was poured into 150 ml of hot water. After cooling, the precipitate was filtered and washed with *n*-hexane to give 4-ethoxy-3-methoxyacetophenone (**7**) with a 96% yield. ^{1}H NMR ($CDCl_3$): δ 1.40 (t, 3H, $J=7$ hz, CH_3), 3.83 (s, 3H, OCH_3), 2.46 (s, 3H, CH_3), 4.03 (q, 2H, $J=7$ Hz, OCH_2), 6.6–7.6 (m, 3H, CH) ppm. IR ($CHCl_3$): ν_{max} 2980, 1715, 1585, 1265 cm^{-1}.

2.2. *4-Ethoxy-3-methoxy-bromoacetylbenzene (**8**)*

To a solution of 4-ethoxy-3-methoxyacetophenone (4.9 g, 25 mmol) in ethyl acetate (50 ml), $CuBr_2$ (30 mmol, 6.7 g) was added. The reaction mixture was poured in water, extracted with ethyl acetate, dried over Na_2SO_4 and evaporated. The residue was crystallized from *n*-hexane:ethyl acetate (1:1 v/v) to five 4-ethoxy-3-methoxy-bromoacetylbenzene (**8**) with a 52% yield. ^{1}H NMR ($CDCl_3$): δ 1.46 (t, 3H, $J=7$ Hz, CH_3), 3.89 (s, 3H, OCH_3), 4.14 (q, 2H, $J=7$ Hz, OCH_2), 4.37 (s, 2H, CH_2Br), 6.6–7.6 (m, 3H, CH) ppm. IR ($CHCl_3$): ν_{max} 2935, 1715, 1585, 1265 cm^{-1}.

2.3. *4-Ethoxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone (**9a**)*

To a solution of 4-ethoxy-3-methoxy-bromoacetylbenzene (3.24 g, 11.8 mmol) and 2-methoxyphenol (1.38 g, 11.8 mmol), in DMF (40 ml), K_2CO_3 (2 g, 15 mmol) was added under magnetic stirring at 25 °C. After 2 h the reaction mixture was poured into 200 ml of hot water. After cooling, the precipitate was filtered and washed with *n*-hexane to give 4-ethoxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone with a 92% yield. ^{1}H NMR ($CDCl_3$): δ 1.46 (t, 3H, $J=7$ Hz, CH_3), 3.83 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.13 (q, 2H, $J=7$ Hz, OCH_2), 5.24 (s, 2H, CH_2CO), 6.7–7.8 (m, 7H, CH) ppm. IR ($CHCl_3$): ν_{max} 2920, 1685, 1590 cm^{-1}.

2.4. *4-Ethoxy-3-methoxy-2-(2,6-dimethoxyphenoxy)-acetophenone (**9b**)*

To a solution of 4-ethoxy-3-methoxy-bromoacetylbenzene (3.24 g, 11.8 mmol) and 2,6-dimethoxyphenol (1.83 g, 11.8 mmol) in DMF (40 ml), K_2CO_3 (2 g, 15 mmol) was added under magnetic stirring at 25 °C. After 2 h the reaction mixture was poured into 200 ml of hot water. After cooling, the precipitate was filtered and washed with *n*-hexane to give 4-ethoxy-3-methoxy-2-(2,6-dimethoxyphenoxy)-acetophenone with a 94% yield. ^{1}H NMR ($CDCl_3$): δ 1.46 (t, 3H, $J=7$ Hz, CH_3), 3.78 (s, 6H, OCH_3), 3.90 (s, 3H, OCH_3), 4.13 (q, 2H, $J=7$ Hz, OCH_2), 5.11 (s, 2H, CH_2CO), 6.4–7.8 (m, 6H, CH) ppm. IR ($CHCl_3$): ν_{max} 3040, 2975, 1670, 1590, 1415, 1250 cm^{-1}. MS: *m/z* 346 (M^+, 21%), 180 (11), 179 (100), 165 (9), 153 (13), 152 (9), 151 (38), 137 (25), 123 (8), 122 (7), 110 (5), 108 (4), 107 (5), 95 (5), 94 (4), 93 (5), 77 (6).

2.5. *1-(4-Ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanone (**10a**)*

To a solution of 4-ethoxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone (1.0 g, 3 mmol) in dimethyl sulfoxide (DMSO) (10 ml), K_2CO_3 (500 mg, 3.6 mmol) and 37% HCHO (6 mmol, 5 ml) were added at 25 °C under magnetic stirring. After 10 min the reaction mixture was poured into water, extracted in ethyl acetate and evaporated under reduced pressure. The product was purified on column chromatography using *n*-hexane:ethyl acetate (1:1) as eluent to give 1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy-3-hydroxy-1-propanone with a 90% yield. ^{1}H NMR ($CDCl_3$): δ 1.44 (t, 3H, $J=7$ Hz, CH_3), 3.77 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.13 (q, 2H, $J=7$ Hz, OCH_2), 3.8–4.3 (m, 3H, H_β, H_γ), 6.4–7.8 (m, 7H, CH) ppm. IR ($CHCl_3$): ν_{max} 3490, 2945, 1655 cm^{-1}. MS: *m/z* 328 (M^+-18, 4%), 317 (5), 316 (23), 180 (11), 179 (100), 177 (5), 151 (65), 149 (6), 137 (25), 123 (18), 122 (19), 108 (9), 95 (8), 94 (7), 92 (12), 79 (10), 77 (25), 65 (12), 63 (7), 52 (10), 51 (10).

2.6. *Reactions of **9a** and **10b** with singlet oxygen*

A 3×10^{-3} M solution of the substrate in acetonitrile (10 ml) containing 5×10^{-4} M Bengal Rose was irradiated in a Pyrex tube surrounded by a Pyrex water jacket connected to a Haake D9-G thermostat to maintain the temperature at 13.0 ± 0.1 °C. The Pyrex tube was dipped into a 1% (w/v) solution of $NaNO_2$ in order to cut off the irradiation at 400 nm. The solution was previous saturated with bubbling oxygen for 1 h. The irradiation was performed by using a 50 W tungsten–halogen lamp. After 8 h, the mixture was analysed by GC–MS and then chromatographed on silica gel using *n*-hexane–ethyl acetate mixtures as eluent.

*2,6-Dimethoxyphenol (**11**).* *m/z* 155 (9%), 154 (91), 153 (2), 140 (7), 139 (71), 138 (5), 137 (7), 125 (8), 112 (7), 111 (100), 110 (11), 109 (10), 108 (18), 107 (16), 97 (8), 96 (97), 95 (30), 94 (8), 93 (64), 83 (7), 82 (6), 81 (22), 80 (10), 79 (28), 77 (9), 69 (6), 68 (48), 67 (10), 65 (41), 63 (10), 62 (6), 55 (20), 53 (32), 52 (21), 51 (30), 50 (20), 42 (5), 40 (6), 39 (43), 38 (10)k 37 (6).

*2-(4-Ethoxy-3-methoxyphenyl)-2-oxo-acetaldehyde (**12**).* ^{1}H NMR ($CDCl_3$): δ 9.79 (s, 1H, CHO), 7.85 (d, 1H, aromatic proton), 7.55 (m, 2H, aromatic proton), 4.03 (q, 2H, $J=7$ Hz, OCH_2), 3.84 (s, 3H, OCH_3), 1.40 (t, 3H, $J=7$ Hz, CH_3) ppm. MS: *m/z* 208 (5%), 180 (9), 179 (63), 152 (10), 151 (100), 123 (33), 122 (8), 120 (8), 108 (18), 92 (8), 80 (8), 79 (23), 76 (6), 67 (6), 65 (13), 62 (6), 53 (6).

4-Ethoxy-3-methoxyacetophenone (7). m/z 195 (5%), 194 (30), 179 (18), 152 (9), 151 (100), 123 (15), 108 (5), 91 (5), 79 (10), 77 (8), 65 (8), 63 (6), 52 (5).

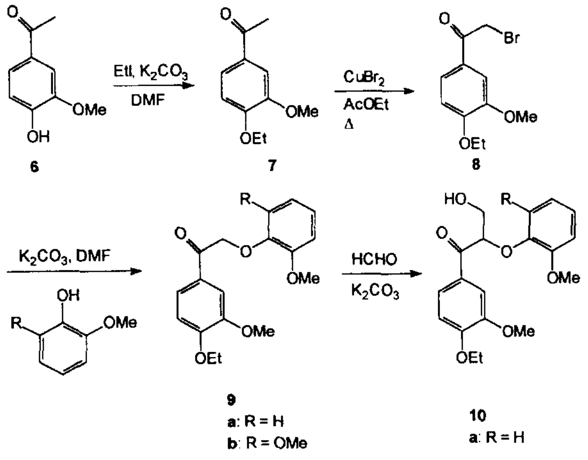
1-(4-Ethoxy-3-methoxyphenyl)-2,3-dihydroxy-1-propanone (13). ^{1}H NMR (CD_3OD): δ 6.6–7.6 (m, 3H, aromatic protons), 4.56 (t, 1H, J=4.5 Hz, CHOH), 4.14 (q, 2H, J=7 Hz, OCH_2), 3.81 (s, 3H, OCH_3), 3.41 (d, 2H, J=4.5 Hz, CH_2OH), 1.42 (t, 3H, J=7 Hz, CH_3) ppm. MS: m/z 222 (3%), 180 (7), 179 (66), 152 (9), 151 (100), 123 (31), 108 (18), 93 (5), 92 (6), 91 (5), 80 (8), 79 (16), 77 (9), 76 (5), 67 (6), 65 (11), 63 (9), 52 (9), 51 (13), 43 (20).

3. Results and discussion

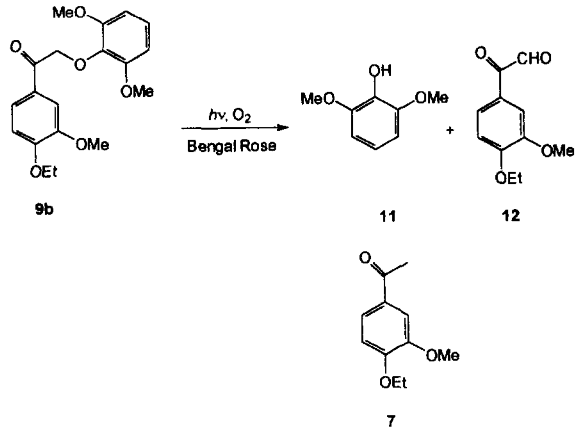
To carry out our experiments on the photodegradation of lignin by singlet oxygen we used two model compounds, the acetophenone derivative **9b** and the β-hydroxypropiophenone derivative **10a**. The synthetic scheme used to prepare these compounds is outlined in Scheme 1.

In order to perform the photochemical oxidation of **9b** and **10a** we used visible-light irradiation of the substrates in acetonitrile in the presence of both oxygen and Bengal Rose, a known singlet oxygen sensitizer [8]. We also used a filter solution to avoid direct absorption of light and we carried out all the photochemical reaction at 13 °C to avoid thermal rearrangements of the products. After 8 h irradiation, the mixtures were analyzed by GC–MS showing the following results. First, we performed the irradiation of **9b** in the presence of oxygen without the sensitizer. We could see that, when direct absorption at 300–350 nm was avoided, no reaction occurred. This experiment allowed us to establish that all the reactions observed in the following experiments are due to the presence of singlet oxygen in the reaction mixture.

The irradiation of **9b** in the presence of 5×10^{-4} M Bengal Rose showed the formation of some degradation products with about 15% yields (Scheme 2, Table 1).



Scheme 1.



Scheme 2.

Table 1
Photochemical oxidation of **9b** and **10a**

Substrate	Product	Yields (%)
9b	**11**	5
	12	3
	7	7
10a	**13**	75

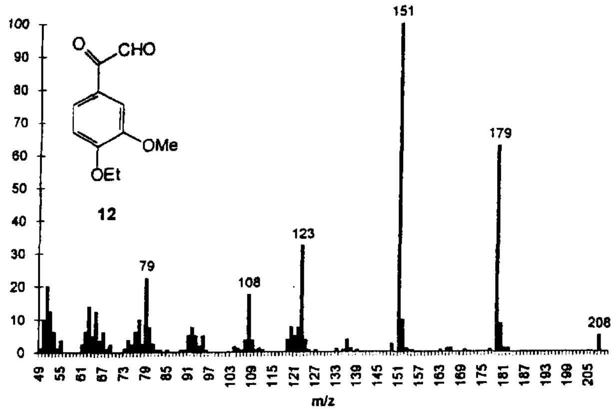
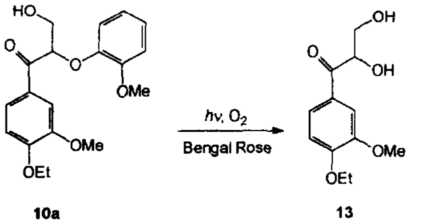


Fig. 1. Mass spectrum of **12**.

The main products obtained are reported in Scheme 2 and were obtained in a 2:1:3 ratio. Compounds **7** and **11** were identified on the basis of their mass spectra by comparison with an authentic samples. The mass spectrum of **12** is reported in Fig. 1. Compound **12** can be recognized by its mass spectrum (Fig.1); the peaks at m/z=208 (M^+), 179 (M^+ − CHO), and at m/z= 151 (M^+ − COCHO) are diagnostic for **12**. Furthermore, the ^{1}H NMR spectrum is in agreement with the proposed structure. In particular we obtained a peak at δ=9.79 ppm that is in agreement with the presence of an aldehydic proton.

We can see that also in this case β-C–O cleavage occurred but the Norrish type II reaction cannot occur as primary photochemical step; on the contrary, it is the result of a reaction of singlet oxygen on **9b**.

This behavior was confirmed when **10a** was used as starting material in the singlet oxygen photo-oxidation reaction. In fact, irradiation under the same conditions described above gave with high conversion yields (70–80%) **13** (Scheme 3).



Scheme 3.

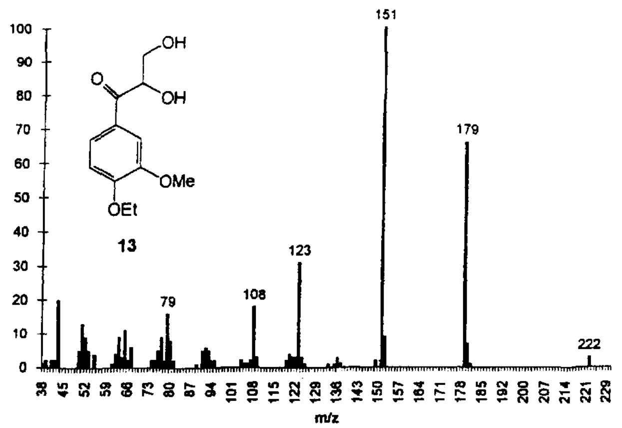


Fig. 2. Mass spectrum of **13**.

The mass spectrum of **13** (Fig. 2) is consistent with the above-described structure. In fact, we observed a peak at $m/z = 222$, assigned at $M^+ - 18$, and peaks at $m/z = 179$, 151, 123 and 108 that can be easily assigned to $M^+ - CH(OH)CH_2OH$, $CH_2{=}CH_2$, CH_3 and $M^+ - COCH(OH)CH_2OH$, respectively. Also in this case, the ^1H NMR spectrum of **13** is in agreement with the proposed structure. In fact, we can observe peaks at $\delta = 4.65$ and 3.41 ppm that are consistent with the presence of the diol. It is noteworthy that, in this case, no phenolic product was observed. Probably, the phenolic product obtained via a ν-C–O cleavage was completely oxidized during the irradiation.

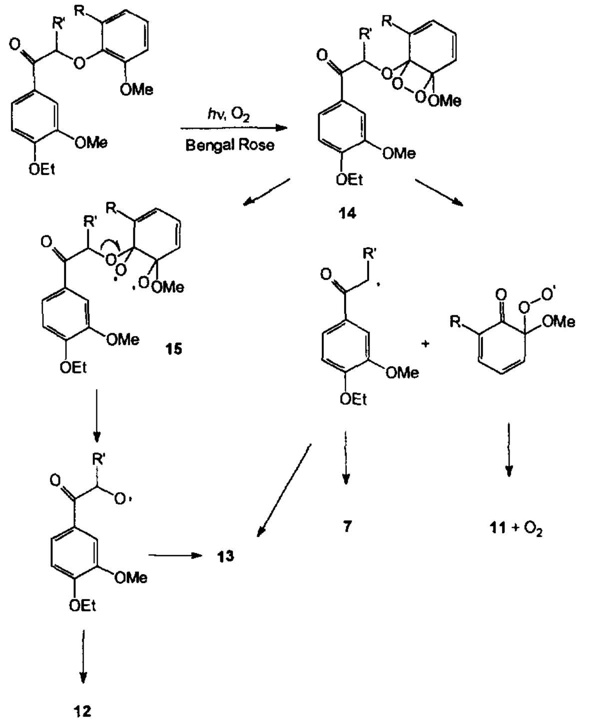
The observed behavior can be explained by assuming that singlet oxygen can react with the aromatic ether part in the substrates. It is known, in fact, that singlet oxygen can react with polymethoxybenzenes to give the corresponding oxidation products via the formation of the 1,2- or the 1,3-endoperoxide [9–13].

The observed high reactivity of **10a** can be explained by assuming that the presence of a hydroxy group can stabilize the endoperoxide intermediate through the formation of an intramolecular hydrogen bond.

Furthermore, the products obtained can be explained considering that the reaction of aromatic ethers with singlet oxygen can produce both C_{arom}–O and C_{alk}–O cleavage [14–16].

In Scheme 4 we have collected our hypothesis about the formation of **7** and **11**–**13**. The endoperoxide **14** can evolve via the formation of the biradical **15** that gives an alkoxy radical and then **12** and **13**; alternatively, C_{alk}–O cleavage can account for the formation of **7** and **11**.

In conclusion we have shown that reactions usually explained by a Norrish II process due to the direct light absorption from the substrate can also be obtained through oxidation reactions induced by singlet oxygen. In a previous article on this subject (see above), singlet oxygen is usually invoked to justify the oxidation of phenolic products deriving from β-C–O cleavage to quinones. The above-reported results seem to indicate that singlet oxygen can play an important role in the photodegradation of lignin, inducing the β-C–O cleavage of the substrates.



Scheme 4.

Acknowledgments

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