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Singlet Oxygen in the Photodegradation of Lignin Models

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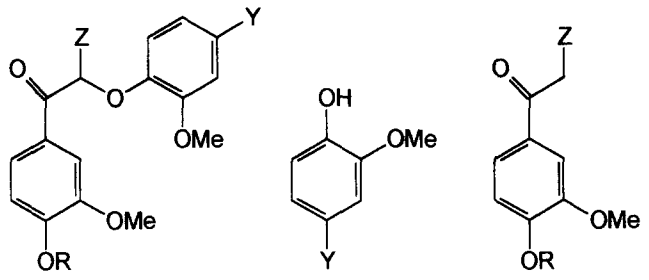
Abstract - The photochemical oxidation of lignin models in the presence of singlet oxygen was studied. The treatment of the non-phenolic β-O-4 aryl ether derivatives **6**, **7**, and **8** in the presence of both oxygen and Rose Bengal gave products deriving from a formal β-C-O cleavage formation. By this way, the derivatives **12**, **13**, and **15** were obtained. The photochemical oxidation of the phenolic β-O-4 aryl ehter **9** gave the same type of product confirming that, in this case, the presence of the carbonyl group is not indispensable to have the cleavage reaction. The use of the model compound **10** showed that, when the phenoxy part of the molecule shows a lower reactivity towards singlet oxygen, the oxidation of the phenol moiety to hydroquinone can occur. The photochemical behaviour of these model compounds can be rationalised from a reaction of singlet oxygen with the phenoxy part of the molecule.

Lignin is a three dimensional phenylpropanoid polymer mainly linked by ether bonds between monomeric phenylpropane units most of which are not readily hydrolyzable. In view of the renewed interest in alternative pulping and bleaching processes, required by environmental concerns,[1-4] in a research program devoted to study the potential use of photochemical methodologies in the setting-up of low environmental impact processes, we studied the capability of singlet oxygen to perform the degradation of lignin models.

The photochemical behaviour of lignin models has been studied considering only the interaction of the ultraviolet light with the molecules in order to explain the color reversion upon exposure to light of the high yield pulps. In these studies, the irradiation of **1** 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.[5-8]

In these experiments a β-C-O cleavage was considered a primary photochemical step, occurring in the first excited singlet or triplet state of **1** to give the phenacyl radical.[9-11] On the contrary, there is no datum on the interaction between singlet oxygen and lignin.

In this paper we want to show that singlet oxygen could be used to obtain the degradation of both hardwood and softwood lignin. This method could be used in order to perform the degradation of the lignin wastes and/or to recycle the products obtained as fine chemicals.



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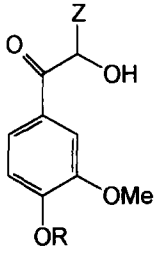

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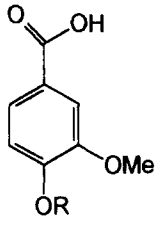

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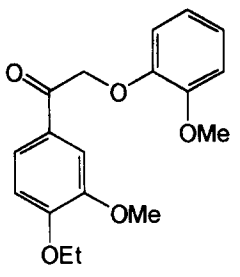
Results and Discussion

In order to investigate the possibility of photodegradation of lignin by singlet oxygen we used several β-O-4 aryl ether model compounds resembling the fundamental bonding patterns of lignin. In particular, the non-phenolic models **6**, **7**, and **8** are representative of fully etherified "core lignin" oxidised in the α position, **6** and **8** being softwood-like models (2'-methoxyphenoxy derivatives) and **7** being a hardwood-like model compound (2',6'-dimethoxyphenoxy derivative). Phenolic compounds **9** and **10**, characterized also by the presence of the typical C_3 lignin side chain, are representative of both softwood and hardwood end-chain lignin moieties, respectively. Under standard oxidation conditions such phenolic substructures constitute the most readily degradable portion in lignin.



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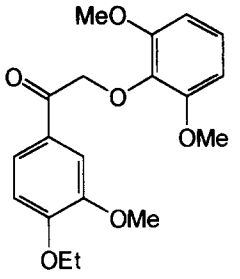

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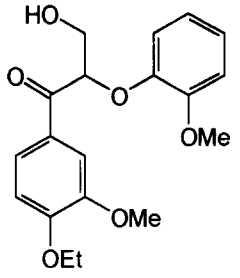

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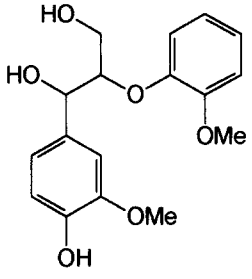

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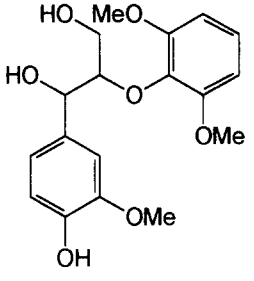

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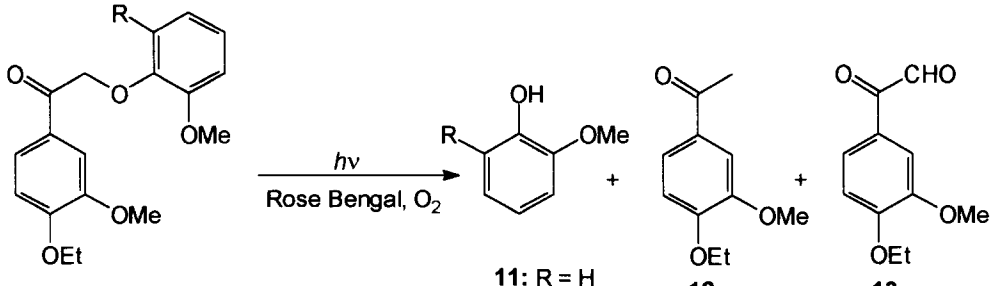
In order to perform the photochemical oxidation of **6-10** we used the irradiation with visible light of the substrates in acetonitrile in the presence of both oxygen and Rose Bengal, a known singlet oxygen sensitizer.[12] We used also a filter solution to avoid direct absorption of light and we carried out all the photochemical reactions at 13°C to avoid thermal rearrangements of the products. After 8-14 h irradiation, the mixtures were analysed by GC-MS showing the following results.

First, we performed the irradiation of **6** 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 were due to the presence of singlet oxygen in the reaction mixture.



6: R = H

11: R = H
14: R = MeO

12

13

The irradiation of **6** in the presence of Bengal Rose as sensitizer gave 2-methoxyphenol (**11**) as the main product (51%), while the other products were 3-methoxy-4-ethoxyacetophenone (**12**) (8%) and (3-methoxy-4-ethoxy-2-phenyl)-2-oxoacetaldehyde (**13**) (15%).

Compounds **12** and **13** were identified on the basis of their mass spectra by comparison with authentic samples.

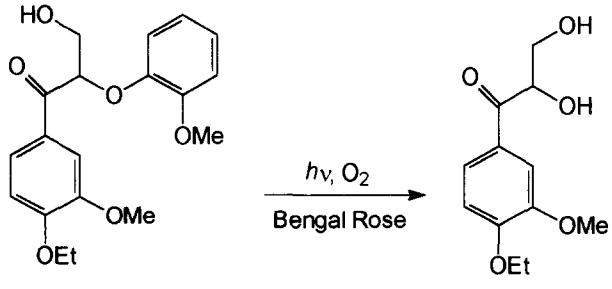
The above reported results show that singlet oxygen can attack lignin model compounds. Interestingly, we have to note that the products are the same described for a β-C-O cleavage induced by direct irradiation of the substrate. In our case, the β-C-O cleavage, a Norrish type II reaction, can not occur as primary photochemical step, but is the result of a reaction of singlet oxygen on **6**.

To confirm this datum, we performed the irradiation of the β-O-4 (2',6'-dimethoxyphenyl ether) **7** in the presence of 5 X 10^{-4} *M* Rose Bengal. Under these experimental conditions **7** was degraded in ca. 15% extent.

The main products (**14**, **12**, and **13**) were in a 2:1:3 ratio, respectively. In this case, the same β-C-O cleavage reaction occurred. However, the reactivity of the substrate was lower than in the previous case. The observed different behaviour of compounds **6** and **7**, which differ only in the absence or the presence of a methoxy group in the C_6' position respectively, can be due to the different reactivity of the phenoxy part of the molecules towards singlet oxygen.

It is noteworthy that, while in direct irradiation Norrish type II reaction occurred in the ketonic part of the molecule, in this case, the reactivity of the substrates can be understood assuming that the phenoxy part of the molecule is responsible for the reactivity towards singlet oxygen.

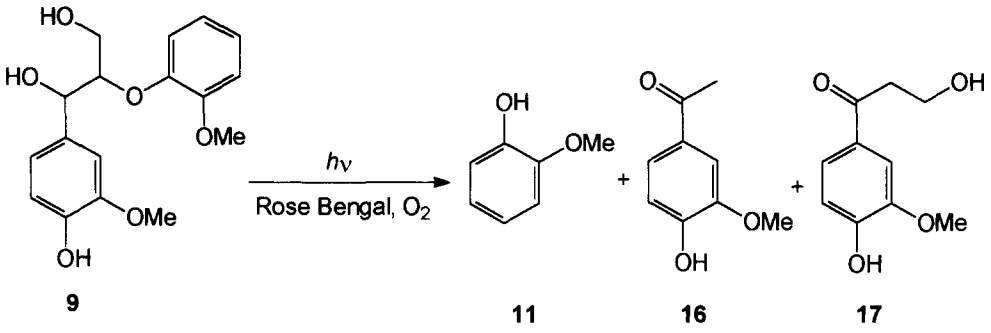
This behaviour was confirmed when **8** was used as starting material in the singlet oxygen photooxidation reaction. In fact, the irradiation under the same conditions described above gave the compound **15** in high conversion yields (70-80%).



8 **15**

In this case, no phenolic product was observed. Probably, it could have been completely oxidised during the irradiation.

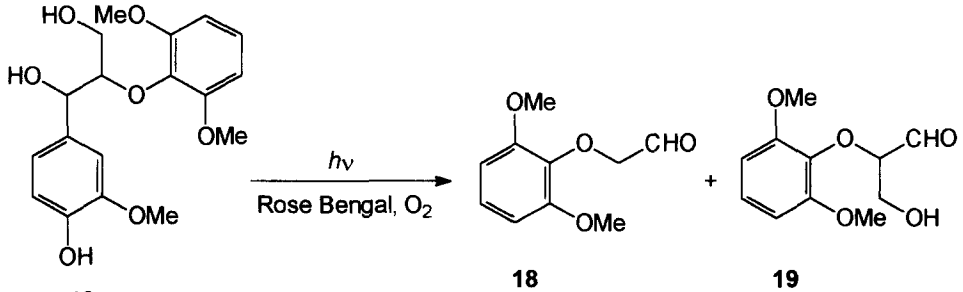
Our attention was then focused on the photochemical reactivity of the phenolic compounds **9** and **10**. Since these lignin models do not show the carbonyl group, we wanted to verify whether the same type of reactions could be observed also in this case. After the irradiation of the compound **9** in acetonitrile in the presence of both oxygen and Rose Bengal, we observed the formation of the phenol **11** (15%), acetovanillone (**16**) (30%) and 1-(3-methoxy-4-hydroxyphenyl)-3-hydroxy-1-propanone (**17**) (28%).



9 **11** **16** **17**

This result is in agreement with the above reported data, showing that the reactivity of singlet oxygen towards this type of molecules is due to an attack on the phenoxy moieties. In fact, in this case, the absence of the carbonyl group did not affect the reactivity of the substrate. It is noteworthy that the presence of an easily oxidizable phenolic function in **9** did not modify the reactivity pattern of the substrate. Probably, the attack of singlet oxygen on the phenoxy part of the molecule is more easy than the oxidation of the phenolic moiety.

Compound **10** showed a different behaviour. In fact, the irradiation of **10** in the presence of oxygen and Rose Bengal gave (2,6-dimethoxyphenoxy)acetaldehyde (**18**) (53%) and 2-(2,6-dimethoxyphenoxy)-3-hydroxy-propanal (**19**) (41%).



10 **18** **19**

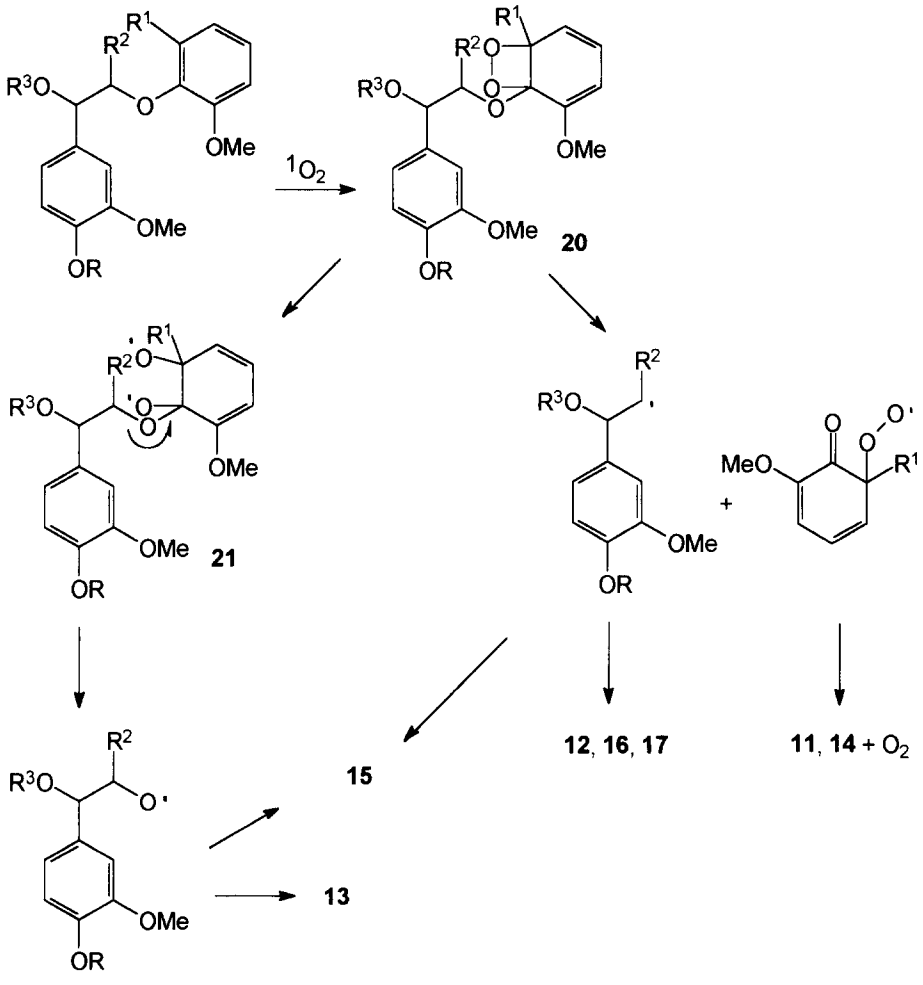
The reactivity of the phenoxy part, in agreement with the above reported results, was found depressed and the photochemical reaction occurred on the phenolic moiety. In this case, the known reactivity of phenols

towards singlet oxygen to give quinones and the subsequent oxidation products can account for the observed reactivity.

Finally, in order to establish if singlet oxygen was involved in the above described reactions, all of them were repeated in the presence of one equivalent of DABCO, a singlet oxygen quencher.[13] Under these photochemical conditions all the reactions were quenched.

The observed behaviour can be explained 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 1,4 endoperoxide.[14-18]

Scheme 1



The occurrence of the products obtained could be rationalised considering that the reaction of aromatic ethers with singlet oxygen can produce both C_{arom}-O and C_{alk}-O cleavage.[19-21]

In Scheme 1 we have collected our hypothesis about the formation of compounds **11**, **12**, **13**, **14**, **15**, **16**, and **17**. The endoperoxide **20** can evolve *via* the formation of the biradical **21** that gives an alkoxy radical and, then, the compounds **13**, **15**, and **17**; alternatively, C_{alk}-O cleavage can account for the formation of compounds **11**, **12**, **14**, and **16**.

In a previous article on this subject singlet oxygen was invoked to justify the oxidation of phenolic products deriving from β-C-O cleavage to quinones.[22] The above reported results seem to indicate that singlet oxygen can play an important role in the photodegradation of lignin inducing a reaction similar to the β-C-O cleavage of the substrates. Furthermore, this "β-C-O cleavage" is independent on the presence of the carbonyl group. In non-phenolic lignin model compounds singlet oxygen reacted with the phenoxy part of the molecule. The softwood-like lignin models **6** and **8** (2'-methoxyphenoxy derivatives) showed an higher reactivity with respect to hardwood-like model **7** (2',6'-dimethoxyphenoxy derivative). This behaviour allows to suggest a more effective action of singlet oxygen on softwood than on hardwood pulping and bleaching processes. The phenolic lignin models showed an interesting reactivity pattern. The softwood-like model **9** reacted with singlet oxygen by oxidation of the phenoxy moiety in the same fashion showed by non-phenolic models **6**, **7**, and **8**. The hartwood-like model **10** showed, in agreement with the non-phenolic analogous **7**, a depression in the reactivity of the phenoxy moiety. In this case singlet oxygen reacted with the phenolic part of the molecule. Finally, the reactivity of compound **10** can be explained assuming an oxidation reaction of the phenol to quinone followed by fragmentation of the substrate.

Experimental

4-Ethoxy-3-methoxyacetophenone - To a solution of acetovanillone (4.15 g, 25 mmoles) in DMF (40 ml), K_2CO_3 (1.15 eq., 4 g) and ethyl iodide (1.5 eq., 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 precipitare was filtered and washed with *n*-hexane to give 4-ethoxy-3-methoxyacetophenone in 96% yield. ^{1}H-NMR ($CDCl_3$) δ: 1.40 (t, 3 H, J = 7 Hz, CH_3), 3.83 (s, 3 H, OCH_3), 2.46 (s, 3 H, CH_3), 4.03 (q, 2 H, J = 7 Hz, OCH_2), and 6.6 - 7.6 ppm (m, 3 H, CH); IR ($CHCl_3$) ν_{max}: 2980, 1715, 1585, and 1265 cm^{-1}. MS, *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).

4-Ethoxy-3-methoxy-bromoacetylbenzene - To a solution of 4-ethoxy-3-methoxyacetophenone (4.9 g, 25 mmoles) in ethyl acetate (50 ml), $CuBr_2$ (30 mmoles, 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 crystallised from *n*-hexane/ethyl acetate (1:1 v:v) to five 4-ethoxy-3-methoxy-bromoacetylbenzene in 52% yield. ^{1}H-NMR ($CDCl_3$) δ: 1.46 (t, 3 H, J = 7 Hz, CH_3), 3.89 (s, 3 H, OCH_3), 4.14 (q, 2 H, J = 7 Hz, OCH_2), 4.37 (s, 2 H, CH_2Br), and 6.6-7.6 ppm (m, 3 H, CH); IR ($CHCl_3$) ν_{max}: 2935, 1715, 1585, and 1265 cm^{-1}.

4-Ethoxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone (**6**) - To a solution of 4-ethoxy-3-methoxy-bromoacetylbenzene (3.24 g, 11.8 mmoles) and 2-methoxyphenol (1.38 g, 11.8 mmoles) in DMF (40 ml) K_2CO_3 (2 g, 15 mmoles) 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 in 92% yield. ^{1}H-NMR ($CDCl_3$) δ: 1.46 (t, 3 H, J = 7 Hz, CH_3), 3.83 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 4.13 (q, 2 H, J = 7 Hz, OCH_2), 5.24 (s, 2 H, CH_2CO),and 6.7-7.8 ppm (m, 7 H, CH); IR ($CHCl_3$) ν_{max}: 2920, 1685, and 1590 cm^{-1}.

4-Ethoxy-3-methoxy-2-(2,6-dimethoxyphenoxy)-acetophenone (**7**) - To a solution of 4-ethoxy-3-methoxy-bromoacetylbenzene (3.24 g, 11.8 mmoles) and 2,6-dimethoxyphenol (1.83 g, 11.8 mmoles) in DMF (40 ml), K_2CO_3 (2 g, 15 mmoles) 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 in 94% yield. ^{1}H-NMR ($CDCl_3$) δ: 1.46 (t, 3 H, J = 7 Hz, CH_3), 3.78 (s, 6 H, OCH_3), 3.90 (s, 3 H, OCH_3), 4.13 (q, 2 H, J = 7 Hz, OCH_2), 5.11 (s, 2 H, CH_2CO), and 6.4-7.8 ppm (m, 6 H, CH); IR ($CHCl_3$) ν_{max}: 3040, 2975, 1670, 1590, 1415, and 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).

1-(4-Ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanone (**8**) - To a solution of 4-ethoxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone (1.0 g, 3 mmoles) in DMSO (10 ml) K_2CO_3 (500 mg, 3.6 mmoles) and 37% HCHO (6 mmoles, 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 in 90% yield. ^{1}H-NMR ($CDCl_3$) δ: 1.44 (t, 3 H, J = 7 Hz, CH_3), 3.77 (s, 3 H, OCH_3) 3.85 (s, 3 H, OCH_3), 4.13 (q, 2 H, J = 7 Hz, OCH_2), 3.8-4.3 (m, 3 H, Hβ, Hγ), and 6.4-7.8 ppm (m, 7 H, CH); IR ($CHCl_3$) ν_{max}: 3490, 2945, and 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).

4-Benzyloxy-3-methoxyacetophenone - To a solution of acetovanillone (10 mmoles, 1.66 g) in pyridine (15 ml) at 5°C 1.5 ml of benzoyl chloride were added under magnetic stirring. After 10 min 50 ml of hexane were added to the reaction mixture and the precipitate was filtered and crystallised from ethyl acetate/hexane 1:1, in 99% yield. ^{1}H-NMR ($CDCl_3$) δ: 2.59 (s, 3 H, CH_3CO), 3.86 (s, 3 H, CH_3O), 7.2-8.3 (m, 8 H, CH). IR ($CHCl_3$) ν_{max}: 2915, 1720, 1660, 1590, 1495 cm^{-1}.

4-Benzyloxy-3-methoxy-bromoacetylbenzene - To a solution of 4-benzyloxy-3-methoxyacetophenone (10 mmoles, 2.70 g) in 30 ml of a 1:1 $CHCl_3/CCl_4$ mixture cooled at 5°C were added under magnetic stirring 10 mmoles of bromine. After 20 min the cooling was removed and the temperature was gradually raised to 40°C. After 2 h the solvents were evaporated under reduced pressure and the crude product was crystallised from hexane/ethyl acetate 7:3 affording pure 4-benzyloxy3-methoxy-4-bromoacetylbenzene in 69% yield. ^{1}H-NMR ($CDCl_3$) δ: 3.86 (s, 3 H, CH_3O), 4.43 (s, 2 H, CH_2), 7.2-8.3 (m, 8 H, CH). IR ($CHCl_3$) ν_{max}: 2915, 1720, 1660, 1590, 1495 cm^{-1}.

4-Benzyloxy-3-methoxy-2-(2,6-dimethoxyphenoxy)-acetophenone - To a solution of 4-benzyloxy-3-methoxy-bromoacetylbenzene (5 mmoles) and 2,6-dimethoxyphenol (5 mmoles) in 20 ml DMF under magnetic stirring, K_2CO_3 (1 g, 7.5 mmoles) was added at 25°C. After 2 h the reaction mixture was poured into 100 ml of hot water. After cooling the precipitate was filtered and washed with *n*-hexane to give 4-benzyloxy-3-methoxy-2-(2,6-dimethoxyphenoxy)-acetophenone in 95% yield. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (s, 6 H, OCH_3), 3.84 (s, 3 H, OCH_3), 5.22 (s, 2 H, CH_2), 6.5-8.3 (m, 11 H, CH). IR ($CHCl_3$) ν_{max}: 2915, 1720, 1660, 1590, 1495 cm^{-1}.

4-Benzyloxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone - To a solution of 4-benzyloxy-3-methoxy-bromoacetylbenzene (5 mmoles) and 2-methoxyphenol (5 mmoles) in 20 ml DMF under magnetic stirring, K_2CO_3 (1 g, 7.5 mmoles) was added at 25°C. After 2 h the reaction mixture was poured into 100 ml of hot water. After cooling the precipitate was filtered and washed with *n*-hexane to give 4-benzyloxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone in 95% yield. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 5.22 (s, 2 H, CH_2), 6.5-8.3 (m, 11 H, CH). IR ($CHCl_3$) ν_{max}: 2915, 1720, 1660, 1595, 1495 cm^{-1}.

1-(4-Hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-propanone - To a solution of 4-benzyloxy-3-methoxy-2-(2,6-dimethoxyphenoxy)-acetophenone (3 mmoles) in DMSO (10 ml) K_2CO_3 (500 mg, 3.6 mmoles) and 37% HCHO (6 mmoles, 5 ml) were added at 25°C under magnetic stirring. After 10 min the reaction mixture was poured into 1 M NaOH, and kept at 25°C for 1 h. The reaction mixture was then neutralised, extracted with ethyl acetate and evaporated under reduced pressure. The product was purified by flash chromatography using *n*-hexane/ethyl acetate 1:1 as eluent to give 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-

dimethoxyphenoxy)-3-hydroxy-1-propanone in 90% yield. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (s, 6 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.8-4.3 (m, 2 H, Hγ), 5.05 (m, 1 H, Hβ), 6.5-8.3 (m, 6 H, CH). IR ($CHCl_3$) ν_{max}: 3480, 2915, 1660, 1590, 1490 cm^{-1}.

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanone - To a solution of 4-benzyloxy-3-methoxy-2-(2-methoxyphenoxy)-acetophenone (3 mmoles) in DMSO (10 ml) K_2CO_3 (500 mg, 3.6 mmoles) and 37% HCHO (6 mmoles, 5 ml) were added at 25°C under magnetic stirring. After 10 min the reaction mixture was poured into 1 M NaOH, and kept at 25°C for 1 h. The reaction mixture was then neutralised, extracted with ethyl acetate and evaporated under reduced pressure. The product was purified by flash chromatography using *n*-hexane/ethyl acetate 1:1 as eluent to give 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanone in 90% yield. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.8-4.3 (m, 2 H, Hγ), 5.05 (m, 1 H, Hβ), 6.5-8.3 (m, 6 H, CH). IR ($CHCl_3$) ν_{max}: 3480, 2915, 1660, 1590, 1495 cm^{-1}.

1-(4-Hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-propanol (**10**) - A solution of 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-propanone (2 mmoles) dissolved in 5 ml of ethanol was cooled at 5°C and 0.5 g of $NaBH_4$ were added under magnetic stirring. The cooling was removed and the temperature was allowed to slowly raise to 25°C. After 3 h the reaction mixture was diluted with water, the ethanol was evaporated under reduced pressure, the crude reaction mixture was extracted with ethyl acetate and evaporated. Purification by flash chromatography using ethyl acetate/*n*-hexane mixtures as eluent afforded 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-hydroxy-1-propanol in 78% yield. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (s, 6 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.4-4.2 (m, 3 H, Hβ, Hγ), 4.9-5.0 (m, 1 H, Hα), 6.7-7.3 (m, 6 H, CH). IR ($CHCl_3$) ν_{max}: 3480, 2950, 1590, 1495 cm^{-1}.

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanol (**9**) - A solution of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanone (2 mmoles) dissolved in 5 ml of ethanol was cooled at 5°C and 0.5 g of $NaBH_4$ were added under magnetic stirring. The cooling was removed and the temperature was allowed to slowly raise to 25°C. After 3 h the reaction mixture was diluted with water, the ethanol was evaporated under reduced pressure, the crude reaction mixture was extracted with ethyl acetate and evaporated. Purification by flash chromatography using ethyl acetate/*n*-hexane mixtures as eluent afforded 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-hydroxy-1-propanol in 78% yield. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 3.4-4.2 (m, 3 H, Hβ, Hγ), 4.9-5.0 (m, 1 H, Hα), 6.7-7.3 (m, 6 H, CH). IR ($CHCl_3$) ν_{max}: 3480, 2950, 1590, 1495 cm^{-1}.

Reactions with singlet oxygen - A 3 x 10^{-3} *M* solution of the substrate in acetonitrile (10 ml) containing 5 x 10^{-4} *M* Rose Bengal 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 $\pm$ 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 4-8 h, the mixture was analysed by GC-MS and then chromatographed on silica gel by using *n*-hexane/ethyl acetate mixtures as eluent.

2-Methoxyphenol (**11**) - MS, *m/z*: 125 (6%), 124 (81), 110 (7), 109 (100), 81 (41), 53 (8), 52 (4), 51 (4).

2,6-Dimethoxyphenol (**14**) - MS, *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), 37 (6).

4-Ethoxy-3-methoxyacetophenone (**12**) - For the spectroscopic properties see above.

2-(4-Ethoxy-3-methoxyphenyl)-2-oxo-acetaldehyde (**13**) - ^{1}H-NMR ($CDCl_3$) δ: 9.79 (s, 1 H, CHO), 7.85 (d, 1 H, aromatic proton), 7.55 (m, 2 H, aromatic proton), 4.03 (q, 2 H, *J* = 7 Hz, OCH_2), 3.84 (s, 3 H, OCH_3), and 1.40 ppm (t, 3 H, *J* = 7 Hz, CH_3); 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).

1-(4-Ethoxy-3-methoxyphenyl)-2,3-dihydroxy-1-propanone (**15**) -^{1}H-NMR (CD_3OD) d: 6.6 - 7.6 (m 3 H, aromatic protons), 4.56 (t, 1 H, *J* = 4.5 Hz, CHOH), 4.14 (q, 2 H, J = 7 Hz, OCH_2), 3.81 (s, 3 H, OCH_3), 3.41 (d, 2 H, J = 4. 5 Hz, CH_2OH), and 1.42 ppm (t, 3 H. J = 7 Hz, CH_3); 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).

4-Hydroxy-3-methoxyacetophenone (**16**) - ^{1}H-NMR ($CDCl_3$) δ: 7.53 (m, 2 H, aromatic protons), 6.95 (d, 1 H, J = 8 Hz, $C2_{arom}$-H), 6.60 (br s, 1H, OH), 3.91 (s, 3 H, OCH_3), and 2.58 ppm (s, 3 H, $COCH_3$); MS, *m/z*, 167 (10%), 166 (99), 138 (22), 137 (40), 124 (21), 123 (33), 122 (100), 121 (14), 109 (11), 95 (25), 92 (33), 77 (74), 65 (14), 63 (10), 52 (11), 51 (11).

1-(4-Hydroxy-3-methoxyphenyl)-3-hydroxy-1-propanone (**17**) -^{1}H-NMR (CD_3OD) δ: 7.60 (dd, 1 H, J_1 = 8 Hz, J_2 = 2 Hz, $C6_{arom}$-H), 7.54 (d, 1 H, J = 2 Hz, $C2_{arom}$-H), 6.86 (d, 1 H, J = 8 Hz, $C5_{arom}$-H), 4.26 (dt, 1 H, J_1 = 10 Hz, J_2 = 6 Hz, C3-H), 3.99 (dt, 1 H, J_1 = 10 Hz, J_2 = 6 Hz, C3-H), and 3.90 ppm (s, 3 H, OCH_3); MS, *m/z*, 179 (11%), 178 (100), 149 (13), 135 (11), 134 (9), 124 (22), 121 (19), 109 (37), 108 (49), 95 (13), 92 (19), 91 (18), 81 (15), 78 (13), 77 (36), 65 (12), 52 (10), 51 (9).

(2,6-Dimethoxyphenoxy)acetaldehyde (**18**) - ^{1}H-NMR ($CDCl_3$) δ: 9.23 (s, 1 H, CHO), 6.3 - 7.4 (m, 3 H, aromatic protons), 3.93 (s, 2 H, CH_2), and 3.76 ppm (s, 6 H, OCH_3); MS, *m/z*, 197 (11%), 196 (100), 167 (12),

154 (23), 153 (92), 152 (65), 151 (12), 139 (10), 138 (51), 125 (30), 122 (18), 110 (41), 108 (14), 107 (25), 95 (33), 93 (26), 92 (10), 77 (21), 65 (12), 51 (10), 39 (11).

2-(2,6-Dimethoxyphenoxy)-3-hydroxy-propanal (**19**) - ^{1}H-NMR (CD_3OD) δ: 9.25 (s, 1H, CHO). 6.3 - 7.5 (m, 3 H, aromatic protons), 4.2 - 3.7 (m, 3 H), and 3.72 ppm (s, 6 H, OCH_3); MS, *m/z*, 208 (65%), 154 (10), 139 (16), 138 (100), 125 (12), 110 (16), 109 (16), 108 (13), 107 (16), 95 (23), 93 (14), 91 (10).

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