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Immobilised porphyrins in monoterpene photooxidations

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ABSTRACT

Porphyrins were covalently linked to modified Merrifield polymers by chlorosulphonation activation of the porphyrin nucleus. These supported porphyrins were used as photosensitizers to promote singlet oxygen oxidation of monoterpenes with an efficiency that depends on porphyrin structure and the spacer used to link it to the polymer structure. The performance of these photosensitizers was studied. Citronellol and α-terpinene gave the expected singlet oxygen ene addition products. α-Pinene and β-pinene also gave products from non-ene reactions, which is explained by the existence of an alternative radical pathway.

1. Introduction

Singlet oxygen generated from photoexcitation of ground-state triplet oxygen is a convenient reagent for preparing endoperoxides or allylic alcohols [1–3]. Limitations of these reactions using a sensitizer catalyst include the difficulty in isolating the product from the catalyst and the poor stability of the catalyst for large-scale reactions. The incorporation of the sensitizer in an insoluble matrix is a convenient approach to overcome these problems. If the ability to generate $^1O_2$ is not overly affected, then the catalyst is simultaneously protected from destruction, and the efficiency is usually increased [4]. Due to their ability to generate singlet oxygen and their resistance to degradation, porphyrins are known as good photosensitizers in the case of homogeneous reactions [5], but the linkage of porphyrins to polymeric matrices to take advantage of the heterogenation has not been fully and adequately exploited to date. Some work on the incorporation of porphyrins in polymeric matrices to be used as photosensitizers has been described, including the use of a PEG-supported hydroxyphenyl porphyrin [6], a copolymer of styrene and divinylbenzene doped with porphyrins [7] or with adsorbed porphyrin [8], a cationic functionalized polystyrene with ionic porphyrins [9], a hydrogel-bound hematoporphyrin [10], and polystyrene microchannel chips with silica-supported porphyrin [11].

We recently reported efficient singlet oxygen oxidations using heterogeneous photosensitizers prepared by the covalent immobilisation of porphyrins on Merrifield-modified polymers [12]. In this work, we extend our initial study, comparing the activity of new immobilised porphyrins and testing their photooxidation efficiency on monoterpenes.

2. Experimental

2.1. General

All solvents were purified before use according to procedures described in the literature. α-Terpinene (85% purity), citronellol (95% purity), α-pinene (98% purity), β-pinene (99% purity), 2,6-di-*tert*-butyl-4-methylphenol (BHT), Merrifield polymer 1% cross-linked 200–400 mesh, 1,12-diaminododecane, and triphenylposphine were used as purchased from Aldrich. Silicagel type 60 with particle size of 0.035–0.070 μm was purchased from Acros Organics. Porphyrins **2**, **3**, **4**, and **6** were prepared by condensation of pyrrol and the corresponding aldehydes by the nitrobenzene method [13]. Dodecylamino-modified Merrifield polymer (**DAP**) was prepared as described previously [12]. ^{1}H NMR spectra were recorded on a 300-MHz Bruker-AMX spectrometer. All J values are given in Hz. Mass spectra were obtained on a HP 5973 MSD apparatus by electron impact at 70 eV. Elemental analyses were carried out on a Fisons Instruments EA1108-CHNS-0 apparatus. Absorption spectra were measured on a Hitachi U-2001 spectrometer. Gas chromatography was carried out using a Supelcowax (30 m × 0.25 mm) capillary column on a Hewlett–Packard 5890A instrument with a Hewlett–Packard 3396A integrator. Gas chromatography (GC) analyses were run at 50 °C (5 min)/10 °C min^{-1}/200 °C (20 min) for the α-pinene and β-pinene oxidation experiments and at 80 °C (2 min)/20 °C min^{-1}/200 °C (20 min) for the citronellol oxidation experiment, at a detector temperature of 250 °C and an injector temperature of 220 °C.

2.2. Preparation of the photosensitizers (*PS1*–*PS5*)

The **PS1** photosensitizer was prepared as described previously [12]. The polymeric photosensitizers **PS1** to **PS4** were prepared by the following general procedure. At room temperature,

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15 mL of chlorosulphonic acid was added to 213 mg of each porphyrin (**2** to **4**). The solution was stirred for 2 h and then carefully poured over ice to precipitate the porphyrin. The precipitate was filtered, dried, and dissolved with dichloromethane, and the resulting solution was dried with sodium sulphate. The solution was concentrated to 30 mL, after which 10 mL of pyridine was added, followed by 376 mg of the aminoalkylated polymer (**DAP**). The mixture was stirred overnight at 30 °C, filtered, and washed with dichloromethane, tetrahydrofuran, methanol, and dichloromethane again. Nonbonded porphyrin was eliminated with these washings. After the solid was dried under vacuum, elemental analysis was carried out to determine the porphyrin incorporation in each of the polymeric photosensitizers **PS2** to **PS4**.

For **PS5**, the same procedure was followed but using the same amount of Merrifield polymer instead of DAP.

2.3. Photooxidation experiments

2.3.1. General procedure

Photooxidation experiments were carried out at room temperature using a laboratory-built photoreactor consisting of three halogen 50 W lamps regularly placed around the reaction flask. The reactions were done in a 100-mL flask equipped with a water condenser and an air inlet. The solutions in $CHCl_3$ were irradiated, with a stream of air continuously flowing through the flask. Then the reaction mixture was filtered to recover the sensitizer, and the filtrate was evaporated to dryness. Typical experiments are described for different substrates with a sensitizer-to-substrate ratio of 1/5000.

2.3.2. α-Terpinene (**7**)

The substrate (4.9 mmol) in 65 mL of chloroform was mixed with the appropriate amount of photosensitizer (9.8×10^{-4} mmol of porphyrin or supported porphyrin) to originate the 1/5000 molar ratio of sensitizer to substrate, and 203 mg of base (sodium hydrogen carbonate) was added. The evolution of the reaction was monitored by UV–vis spectroscopy at 268 nm, with disappearance of the reagent verified by GC. The photosensitizer was collected by filtration, and the product was obtained by evaporation of the solvent and analysed by ^{1}H NMR. The ^{1}H NMR data were in agreement with those reported previously [14,15].

2.3.3. Ascaridole (**8**)

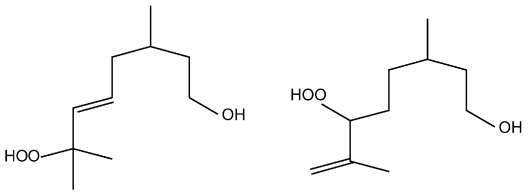
^{1}H NMR (300 MHz, $CDCl_3$): $\delta_H = 0.97$ (3H, d, J 6.90, CH_3), 0.98 (3H, d, J 6.9, CH_3), 1.31 (3H, s, CH_3), 1.51–1.56 (2H, m), 1.85 (H, sept, J 6.90, isopropyl), 1.97–1.92 (2H, m), 6.42 (H, d, J 8.58, olefinic CH), 6.53 ppm (H, d, J 8.58, olefinic CH); MS (EI, 70 eV): m/z 168 (M+, 1%), 150 (7%), 134 (32%), 119 (100%), 107 (33%), 91 (37%).

2.3.4. p-Cymene

^{1}H (300 MHz, $CDCl_3$): $\delta_H = 1.22$ (3H, d, J 1.68, $CH_3^{\cdot}$), 1.24 (3H, d, J 1.68, $CH_3^{\cdot}$), 2.31 (3H, s, $CH_3^{\cdot}$), 2.87 (H, sept, isopropyl), 7.11 (4H, s, Ar-H$^{\cdot}$); MS (EI, 70 eV): $m/z = 134$ (M^+, 30%), 119 (100%), 115 (6%), 103 (4%), 91 (18%), 77 (5%).

2.3.5. Citronellol (**9**)

The substrate (4.9 mmol) in 65 mL of chloroform was mixed with the appropriate amount of photosensitizer (9.8×10^{-4} mmol of porphyrin or supported porphyrin) to originate a sensitizer-to-substrate molar ratio of 1/5000. Then 203 mg of base (sodium hydrogen carbonate) was added. GC was used to monitor the evolution of the reaction after disappearance of the reagent. After filtration of the photosensitizer and evaporation of the solvent, the product was obtained and analysed by ^{1}H NMR. The proportion of the two regioisomers thus obtained, (*E*)-7-hydroperoxy-3,7-dimethyloct-5-en-1-ol (**10**) and 6-hydroperoxy-3,7-dimethyloct-7-en-1-ol (**11**), was estimated by ^{1}H NMR [16].



(**10**) (**11**)

2.3.6. (E)-7-Hydroperoxy-3,7-dimethyloct-5-en-1-ol (**10**)

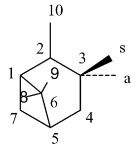
^{1}H NMR (300 MHz, $CDCl_3$): $\delta_H = 0.87$ (d, $J = 6.4$ Hz, 3H, $CHCH_3$), 1.25 ± 1.71 (m, 5H, CH_2CHCH_2), 3.64 (m, 2H, CH_2OH); 1.29 [s, 6H, $COOH(CH_3)_2$], 5.55 (d, $J = 15.8$ Hz, 1H, COOHCH=CH), 5.63 (m, 1H, COOHCH=CH).

2.3.7. 6-Hydroperoxy-3,7-dimethyloct-7-en-1-ol (**11**)

$\delta_H = 0.85$ (d, $J = 6.5$ Hz, 3H, $CHCH_3$), 1.25 ± 1.71 (m, 5H, CH_2CHCH_2), 3.64 (m, 2H, CH_2OH), 1.65 (s, 3H, $CqCH_3$), 1.95 (m, 2H, $COOHCH_2$), 4.24 (m, 1H, CHOOH), 4.95 (s, 2H, $Cq{=}CH_2$). The proportion of the two regioisomers (**10**) and (**11**) was estimated by ^{1}H NMR: % for (**10**) = $[(\text{area}_{\delta_H=5.55} + \text{area}_{\delta_H=5.68})/2] \times 100/[(\text{area}_{\delta_H=5.55} + \text{area}_{\delta_H=5.68})/2 + (\text{area}_{\delta_H=4.95})/2]$.

2.3.8. α-Pinene (**12**) and β-pinene (**13**)

The substrate (9.8 mmol) in 130 mL of chloroform was mixed with the appropriate amount of photosensitizer (1.7×10^{-3} mmol of porphyrin or supported porphyrin) to originate a sensitizer-to-substrate molar ratio of 1/5000, after which 406 mg of base (sodium hydrogen carbonate) was added. The evolution of the reaction was monitored by GC. In the end, the reaction mixture was submitted to reduction with triphenylphosphine, and the products were isolated, as a single fraction, by column GC on silica using CH_2Cl_2 as eluent. Analysis of the product by ^{1}H NMR spectroscopy allowed estimation of the relative yields of *trans*-pinocarveol (**14**) and myrtenol (**15**). The data of the ^{1}H NMR were in agreement with those reported previously [17–20].



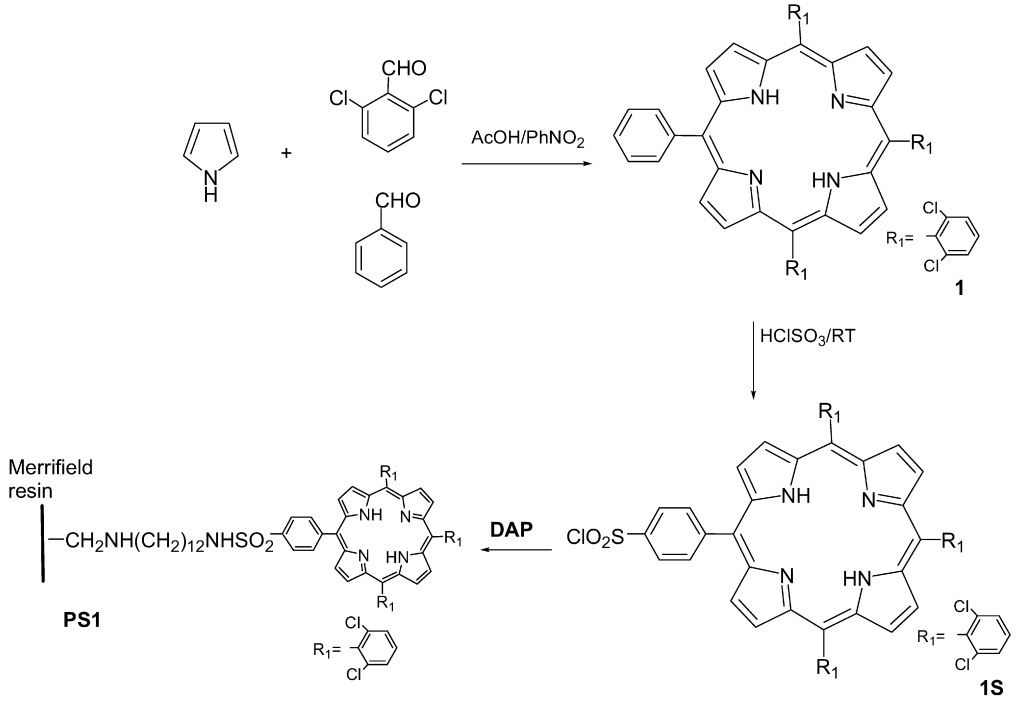
2.3.9. Trans-pinocarveol (**14**)

^{1}H (300 MHz, $CDCl_3$): $\delta_H = 0.64$ (s, 3H, 9-CH_3), 1.27 (s, 3H, 8-CH_3), 1.72 (d, 1H, $J = 9.8$ Hz, 7-H), 1.84 (dd, 1H, $J = 14.6$, 4.2 Hz, 4-Hb); 1.99 (m, 1H, 5-H), 2.23 (m, 1H, 4-Ha), 2.37 (m, 1H, 7-H), 2.51 (t, 1H, $J = 5.5$ Hz, 1-H); 4.42 (d, $J = 7.6$ Hz, 1H, 3-H), 4.82 (s, 1H, 10-Ha), 5.00 (s, 1H, 10-Hb). MS (EI, 70 eV): $m/z = 152$ (M+, 1%), 134 (33%), 119 (40%), 109 (30%), 91 (72%), 92 (100%), 83 (54%), 70 (52%).

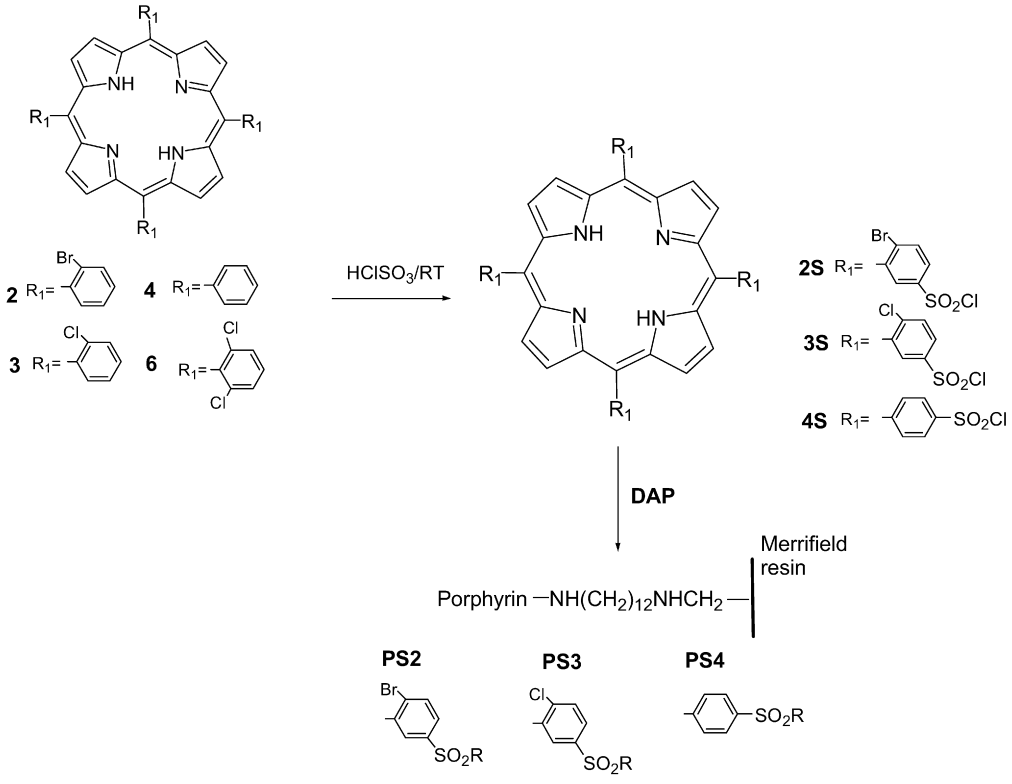
2.3.10. Myrtenol (**15**)

^{1}H (300 MHz, $CDCl_3$): $\delta_H = 0.83$ (s, 3H, 9-CH_3), 1.29 (s, 3H, 8-CH_3), 1.17 (d, 1H, $J = 8.6$ Hz, 7-H), 2.13 (m, 1H, 5-H); 2.13 (m, 1H, 1-H), 2.24 (m, 1H, 4-Ha), 2.27 (m, 1H, 4-Hb); 2.41 (m, 1H, 7-H), 3.98 (m, 2H, 10-H); 5.47 (m, 1H, 3-H). MS (EI, 70 eV): $m/z = 152$ (M+, 4%), 134 (1%), 119 (16%), 108 (31%), 91 (49%), 79 (100%).

The relative amounts of *trans*-pinocarveol (**14**) and myrtenol (**15**) were estimated by ^{1}H NMR: % for (**14**) = $\text{area}_{\delta_H=4.42} \times 100/(\text{area}_{\delta_H=5.47} + \text{area}_{\delta_H=4.42})$.



Scheme 1. PS1 synthesis sequence.



Scheme 2. PS2–PS4 synthesis sequence.

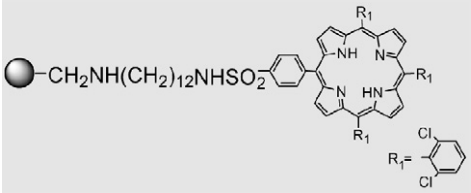
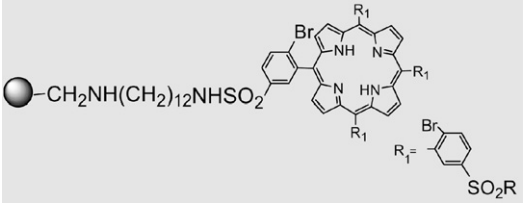
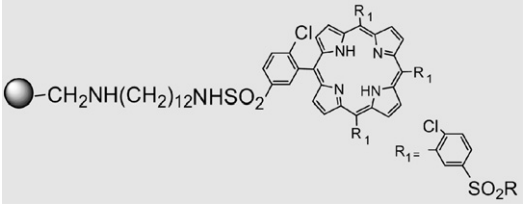
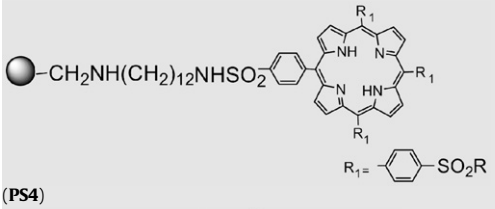
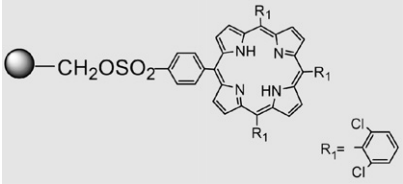
3. Results and discussion

3.1. Synthesis of supported photosensitizers

In our previous report, we established a simple route to covalently link nonsymmetrical porphyrin **1** to a Merrifield polymer structure [12]. The strategy requires the reaction of the Merrifield polymer with an excess of 1,12-diaminododecane to obtain a dodecyl aminopolymer (**DAP**) derivative. The covalent linkage of porphyrin was carried out by controlled chlorosulphonation of **1** followed by the reaction of the corresponding chlorosulphonyl derivatives (**1S**) with **DAP**, thus obtaining photosensitizer **PS1** (Scheme 1).

Because nonsymmetrical porphyrin **1** is obtained in a low yield, we tried to substitute it by symmetrical tetraarylporphyrins **2** to **4**, which are obtained in much higher yields. Following the same strategy as for chlorosulphonation, we obtained tetrachlorosulphonyl derivatives (**2S**–**4S**) instead of monochlorosulphonyl deriva-

Table 1
Values for porphyrin incorporation (mmol g^{-1}) for photosensitizers **PS1** to **PS5**

Polymer–spacer–porphyrin	Values of porphyrin incorporation (mmol g^{-1})
 (**PS1**)	0.04
 (**PS2**)	0.02
 (**PS3**)	0.05
 (**PS4**)	0.04
 (**PS5**)	0.20

tives as in the case of porphyrin **1**. The reaction of these tetrachlorosulphonyl derivatives with a polymer may increase the likelihood of bonding with the aminogroups of **DAP**. Nonbonding chlorosulphonyl groups possibly hydrolyze in the subsequent treatments. Photosensitizers **PS2**–**PS4** were prepared in this manner (Scheme 2).

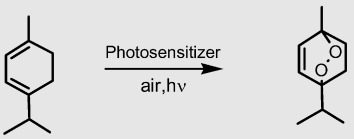
We also attempted the reaction of **1S** directly with the Merrifield polymer, originating photosensitizer **PS5**, which has no spacer between the polymer structure and the porphyrin. We performed comparative studies between our photosensitizers (**PS1**–**PS5**) and tetra (2,6-dichlorophenyl) porphyrin (TDCPP) (**6**), one of the most active sensitisers used in photooxidation [21].

Values for the amount of porphyrin bonded to **DAP** were calculated from the nitrogen content obtained by elemental analysis of polymers **PS1**–**PS4**, discounting the value of nitrogen corresponding to the initial **DAP** polymer. For **PS5**, the porphyrin content was calculated directly from the nitrogen values (Table 1).

Using the tetrachlorosulphonyl derivatives (**2S**–**4S**), we found no increase in the loading of the porphyrins to the amino polymer (**DAP**) compared with the monosulphonyl derivative **1S**, as we would expect from the presence of more chlorosulphonyl groups. With bromo derivative (**2S**), this loading actually was lower. Surprisingly, **PS5** exhibited the highest loading of the photosensitizers tested. In the final washing of **PS5**, we isolated and identified by mass spectrometry a porphyrin with one sulphonic group, certainly due to hydrolysis of the chlorosulphonyl group of **1S**. By infrared spectroscopy, we noted that the band for the CH_2Cl benzylic group (1264 cm^{-1}) was significantly decreased relative to the original Merrifield polymer, suggesting some substitution at this position. Washing with triethylamine in dichloromethane did not reduce this loading value, suggesting a strong bond between porphyrin and polymer. The comparison of the infrared absorption zones for the sulphonic groups [22], 1370–1330 cm^{-1} and 1200–1145 cm^{-1} of the Merrifield polymer and the isolated porphyrin with a sulphonic group, suggests that in this case, a direct bond of porphyrin to polymer structure occurred from displacement of the benzylic chlorine by the free sulphonic group.

Table 2
Results for the photooxidation of α-terpinene with **PS1** to **PS5** and porphyrin **6**

Entry



(**7**) (**8**)

	Photosensitizer	$R = n_{ph}/n_{terp}$ [a]	Time (h)	**8** (%) [b]
1	**PS1**	1/600	2.5	87 (13)
2	**PS2**	1/600	3	92 (8)
3	**PS3**	1/600	3	91 (9)
4	**PS5**	1/600	4	84 (16)
5	**6**	1/600	1.5	88 (12)
6	**PS1**	1/5000	3.5	86 (14)
7	**PS2**	1/5000	4.5	83 (17)
8	**PS3**	1/5000	7	86 (14)
8	**PS4**	1/5000	11	84 (16)
9	**PS5**	1/5000	8.2	66 (34)
10	**6**	1/5000	2.3	93 (7)

[a] Photosensitizer/α-terpinene ratio.
[b] % of **8** in reaction mixture by ^{1}H NMR. In parentheses the amount of *p*-cymene.

3.2. Photooxidation reactions

We began the evaluation of the supported photosensitizers **PS1**–**PS5** by attempting the photooxidation of α-terpinene (**7**) [23] using chloroform as the solvent, air as the oxygen supply, and sensitizer-to-substrate ratios of 1:600 and 1:5000. For supported catalysts, the polymer was filtered at the end of the reaction and the solvent evaporated. For free porphyrin TDCPP (**6**), a chromatographic separation was needed. ^{1}H NMR analysis of the reaction residue showed that the main product was ascaridole (**8**), as was confirmed by GC/MS analysis. Some *p*-cymene was detected by GC/MS and quantified by ^{1}H NMR. The results for **PS1**–**PS5** and TDCPP (**6**) are given in Table 2.

The results in Table 2 show that, compared with porphyrin **6**, the photosensitizers tested exhibited moderate to good activity as singlet oxygen generators. A blank experiment with Merrifield polymer demonstrated no product formation after 13 h of reaction. The different photosensitizers exhibited much the same reactivity order, **6** > **PS1** > **PS2**, **PS3** > **PS5** for the ratio of 1/600 and **6** > **PS1** > **PS2** > **PS3** > **PS5** > **PS4** for the ratio of 1/5000. Photosensitizer **PS5** had lower activity than **PS1**, **PS2** and **PS3**, as was expected based on the absence of the C_{12} chain spacer [12]; however, **PS5** was more active than **PS4**, which had the C_{12} spacer. In this case, we conjecture that the positive effect of the spacer in **PS4** was counter weighed by the absence of the *ortho* halogen atoms in porphyrin structure. These halogens are important to pro-

Table 3
Photooxidation of α-terpinene with **PS1** or porphyrin **6** using different photosensitizer/α-terpinene ratios

Entry	Photosensitizer	$R = n_{ph}/n_{terp}$[a]	Time (h)	**8** (%)[b]
1	**6**	1/600	1.5	88 (12)
2	**6**	1/5000	2.3	91 (9)
3	**PS1**	1/600	2.5	87 (13)
4	**PS1**	1/2000	3.3	95 (5)
5	**PS1**	1/5000	3.3	86 (14)
6	**PS1**	1/15000	4	82 (18)
7	**PS1**	1/30000	10	65 (35)
8	**PS1**	1/60000	19.3	51 (49)

[a] Photosensitizer/α-terpinene ratio.
[b] % of **8** in reaction mixture by NMR. In parentheses the amount of *p*-cymene.

Table 4
Results for consecutive photooxidations of α-terpinene using photosensitizer **PS1**

Reaction	$R = n_{ph}/n_{terp}$[a]	Time (h)	**8** (%)[b]	TOF[c]
1st	1/600	2.5	87 (13)	209
2nd	1/600	2	86 (14)	258
3rd	1/600	2.5	85 (15)	204
1st	1/5000	3.3	86 (14)	1303
2nd	1/5000	3.3	86 (14)	1303
3rd	1/5000	2.5	87 (13)	1740
1st	1/15000	4	82 (18)	3075
2nd	1/15000	8	78 (22)	1463
3rd	1/15000	8.5	81 (19)	1429

[a] **PS1**/α-terpinene ratio.
[b] % of **8** in reaction mixture by NMR. In parentheses figures the amount of *p*-cymene.
[c] Moles of **8**/moles of **PS1** × h.

mote stability of the macrocycle [21] and to activate singlet oxygen generation by the heavy atom effect [24]. The supported catalyst with the spacer and the ortho chlorine atoms, **PS1**, proved to be the most active, with a performance close to that of the nonsupported catalyst **6**. Crude reaction products showed a mass balance corresponding to near quantitative conversions. NMR analysis revealed ascaridole (**8**) as the main product, with varying amounts of *p*-cymene due to ring oxidation of α-terpinene. Table 2 shows that for the photooxidation reaction, selectivity was higher at the 1/600 ratio than at the 1/5000 ratio. Considering that commercial α-terpinene contains about 5% *p*-cymene (by ^{1}H NMR), the supported photosensitizers generally exhibited very good selectivity for the formation of ascaridole **8**. Only in the case of **PS5**, which does not have the C_{12} chain spacer, and at the 1/5000 ratio did we obtain an exceptional amount of *p*-cymene.

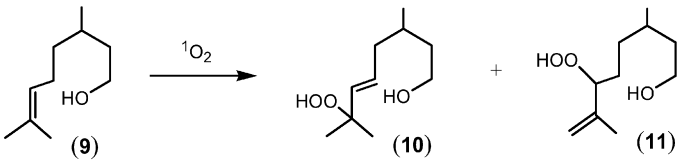
Of all photosensitizers tested, **PS1** showed the best activity. To analyse its photocatalytic ability, we carried out the photooxidation of α-terpinene by increasing the photosensitizer-to-substrate ratio up to 1/60,000 (Table 3). For comparison, we also carried out some reactions with porphyrin **6** with this substrate. The results demonstrate that at photosensitizer-to-α-terpinene ratios of up to 1/15,000, **PS1** showed good catalytic activity, originating mainly the product from singlet oxygen reaction. At a ratio of 1/30,000, the reaction was much slower, and the amount of *p*-cymene increased considerably. At a ratio of 1/60,000 ratio, the yields of the oxygenated product and *p*-cymene were equivalent.

We further studied the efficiency of our supported catalysts after recovery and recycling. We evaluated this efficiency for **PS1** in α-terpinene photooxidation at three different catalyst-to-substrate ratios. The results, given in Table 4, show that for photosensitizer-to-substrate ratios of 1/600 and 1/5000, **PS1** was able to carry out 3 consecutive reactions with no significant loss of activity and with good selectivity for ascaridole (**8**). Turnover frequencies (TOFs) remained the same in the sequential cycles, indicating good catalyst stability. TOF values were higher at higher photosensitizer-to-substrate ratios, reaching a maximum of 3075 at a ratio of 1/15,000. At this photosensitizer-to-substrate ratio, a clear decrease in photosensitizer activity was seen after the first reaction, doubling the reaction time, but the activity for the third consecutive reaction was maintained. This corresponds to 45,000 total reaction cycles, similar to the value obtained with the Griesbeck photooxidation system [16]. With simple filtration of the photosensitizer, about 4.6 g of ascaridole (**8**) could be obtained using only 35 mg of **PS1** after 3 consecutive reactions.

Table 5
Photooxidation of α-terpinene in consecutive experiments with a photosensitizer/α-terpinene ratio of 1/5000

Photosensitizer	Reaction	Time (h)	**8** (%)[a]	TOF[b]
PS1	1st	3.3	86 (14)	1303
	2nd	3.3	86 (14)	1303
	3rd	2.5	87 (13)	1740
PS2	1st	4.5	83 (17)	922
	2nd	5.1	86 (14)	843
	3rd	5.1	84 (16)	823
PS3	1st	7	82 (18)	586
	2nd	8.5	84 (16)	494
	3rd	9	79 (21)	439
PS5	1st	8	66 (34)	413
	2nd	12	63 (37)	263

[a] % of **8** in reaction mixture by ^{1}H NMR. In parentheses figures the amount of *p*-cymene.
[b] Moles of **8**/moles of photosensitizer × h.

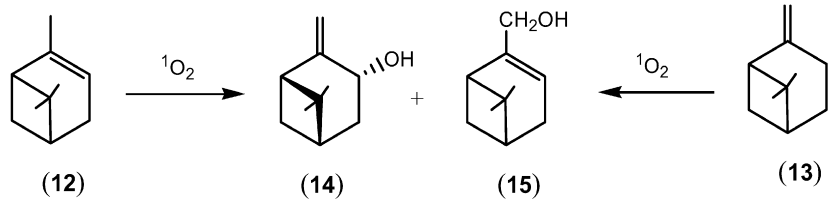


Scheme 3. Citronellol photooxidation products.

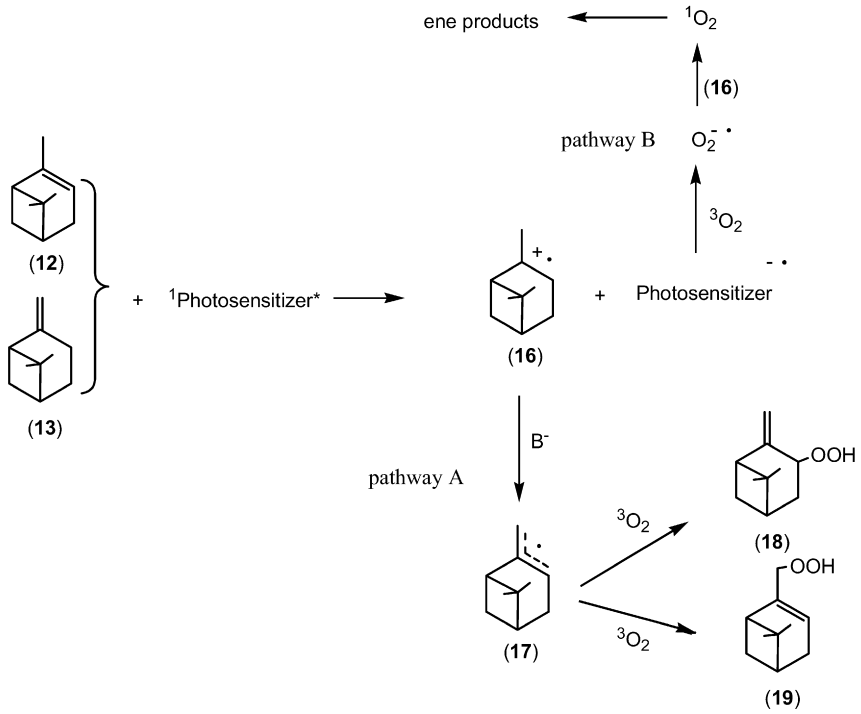
From a practical standpoint, photosensitizers **PS2**, **PS3**, and **PS5** can be prepared more easily than **PS1** and, if sufficiently active, can be considered better solutions for large-scale processes. Table 5 compares the activity of **PS1**, **PS2**, **PS3**, and **PS5** in α-terpinene oxidation and in consecutive reactions. Supported photosensitizers with a C_{12} carbon chain spacer (**PS1**–**PS3**) exhibited almost the same activity during the three reaction cycles. In contrast, the catalyst without the spacer, **PS5**, was the least active, exhibiting a slower second reaction cycle and a greater amount of *p*-cymene. As indicated by its TOF values, **PS1** was the most active photosensitizer, with activity superior to that of **PS2** and **PS3**. The photosensitizer with bromine groups, **PS2**, seemed to be much more active than **PS3** with chlorine atoms. The importance of the spacer can be demonstrated by comparing the results for **PS1** and **PS5**. **PS1** has a porphyrin with similar structure to **PS5**, spaced from the polymer backbone by a C_{12} chain, and is a much more active photosensitizer.

To further investigate the scope of this type of supported photosensitizer, we carried out reactions using other monoterpenes as substrates. Photooxidation of citronellol (**9**) originated the isomeric hydroperoxides (**10**) and (**11**) [25–30], which, after reduction and acid cyclization [31], could be converted to a mixture of *cis* and *trans* rose oxides, which are valuable compounds in the perfume industry (Scheme 3).

With the more active photosensitizers **PS1** and **PS2** and free porphyrin **6**, we attempted photooxidation of citronellol (**9**) using different photosensitizer-to-substrate ratios. The results, given in Table 6, show that citronellol was more difficult to oxidize than α-terpinene, indicating that supported photosensitizers had much slower reactions than free porphyrin but gave the same iso-



Scheme 4. α-Pinene and β-pinene photooxidation products.



Scheme 5. Proposed α-pinene and β-pinene photooxidation reaction mechanism.

Table 6
Results of citronellol photooxidation using supported photosensitizers **PS1** and **PS2** and free porphyrin **6**

Photosensitizer	Photosensitizer/substrate ratio	Reaction time (h)	Isolated yields (%)	Product distribution (%)[a]	
				(**10**)	(**11**)
6	1/600	1.5	99	49	51
6	1/5000	4	99	50	50
PS1	1/600	6.5	98	47	53
PS1	1/5000	10	99	47	53
PS2	1/600	8	99	48	52
PS2	1/5000	25	99	45	55

[a] Calculated from ^{1}H NMR of the crude reaction mixture.

Table 7
Results of α-pinene and β-pinene photooxidations using supported photosensitizers **PS1** and **PS2** and free porphyrins **4** and **6**. Photosensitizer/substrate ratio of 1/5000

Substrate	Entry	Photosensitizer	Time (h)	Products yields (%)[a]	**14** (%)[b]	**15** (%)[b]
(**12**)	1	**6**	20	54	42	58
	2	**4**	18	65	88	12
	3	**PS1**	24	85	69	31
	4	**PS2**	88	55	46	54
	5	**PS1**[c]	29	64	81	19
(**13**)	6	**6**	24	59	34	66
	7	**PS1**	37	53	32	68
	8	**PS2**	138	53	26	74

[a] Isolated yields after reduction.
[b] Estimated from ^{1}H NMR of the isolated product (Section 2).
[c] Photosensitizer/substrate ratio of 1/600.

lated yields. Among the supported photosensitizers, **PS1** again was more active than **PS2**, particularly when higher amounts of substrate relative to catalyst were used. The results in Table 6 indicate a slight excess of allylic hydroperoxide (**11**) in **PS1** and **PS2**, in contrast to other systems in which allylic hydroperoxide (**10**) is favoured [16,29].

Photooxidation of α-pinene (**12**) and β-pinene (**13**) with **PS1**, **PS2**, and **6**, followed by reduction of the corresponding hydroperoxide products with triphenylphosphine [32] and chromatographic isolation, gave *trans*-pinocarveol (**14**) and another product, identified by comparison of the ^{1}H and ^{13}C spectra as myrtenol (**15**) [17–20] (Scheme 4, Table 7).

The results demonstrate that with these latter two monoterpenes, reactions were slower and lower product yields were obtained compared with those obtained with citronellol and α-terpinene and, as expected, β-pinene was less reactive than α-pinene [33]. In both cases, relative to the other substrates, there were some differences considering the formation of different oxidation products. The product expected for the singlet oxygen addition to **12** was *trans*-pinocarveol **14**, and that expected for this addition to **13** myrtenol was **15**, both of which originated from an ene reaction [34]. We also observed products coming from non-ene origin, **15** in the case of α-pinene and **14** in the case of β-pinene. In some cases, these were the main products. A possible explanation for

the appearance of these unexpected products from substrates like α-pinene and β-pinene is a mechanism of electron transfer between excited photosensitizers and these substrates, as proposed by Zhang [33] (Scheme 5).

The electron transfer between **12** or **13** and the excited photosensitizer gave the same radical cation **16** and the radical anion photosensitizer, which can mediate the ene reaction by a superoxide radical via type I photooxygenation (pathway B) [35]. Alternatively, species **16** can lose a proton to the hydrogen carbonate, giving the allyl radical **17**, which, by a radical chain reaction with triplet oxygen, leads to the hydroperoxides **18** and **19**. This corresponds to the non-ene reaction (pathway A) a route supported by some data. Reaction of **PS1** and α-pinene at a low substrate ratio (1/600, entry 5) gave more product from ene addition than the reaction with a higher substrate ratio (1/5000, entry 3). Because electron-transfer processes require proximity between the donor and acceptor species, decreasing the amount of substrate molecules decreases the likelihood of the electron-transfer process. Reaction with porphyrin **4**, which must have a more negative reduction potential than porphyrin **6** [36], disfavoured pathway A, and thus the amount of non-ene products would be expected to be lower, as was seen (entry 2). More compelling evidence that pathway A is operative in these reactions came from the photooxidation of α-pinene with **PS1** in the presence of BHT, a known radical scavenger. The reaction was much slower (64 h) because pathway A was inoperative. After reduction and chromatographic workup, no myrtenol was detected; only the *trans*-pinocarveol was isolated.

4. Conclusion

Heterogeneous catalysts for singlet oxygen generation were prepared from the chlorosulphonation of porphyrins and reaction with amino alkylated Merrifield resin in a very simplified preparation procedure that compares favourably with those reported previously. The sensitizer with chlorine atoms in the porphyrin structure **PS1** proved to be very active for the photooxidation of α-terpinene and citronellol, demonstrating efficiency in higher substrate-to-catalyst ratios, up to 1/30,000. With this catalyst, consecutive reactions could achieve up to 45,000 oxidation cycles. In the case of poorly reactive substrates (i.e., α-pinene and β-pinene), non-ene products were formed through a pathway involving an electron-transfer mechanism.

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