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Photochemical hydroperoxidation of terpenes
I. Synthesis and characterization of α-pinene, β-pinene and limonene hydroperoxides

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Abstract

The photohydroperoxidation of the stereoisomers of three terpenes ((+) and (−) α-pinene, (+) and (−) β-pinene and (+) and (−) limonene) has been performed by using photocatalysts, such as zinc oxide, or sensitizers, such as anthracene or rose Bengal, supported on cross-linked polystyrene. Hydroperoxides accumulated alone in the first stages of sensitized oxidation but were always associated with alcoholic and carbonyl products in the case of ZnO. Secondary products obtained for longer exposure times in sensitized oxidations were identified by gas chromatography/mass spectrometry and mechanisms for their formation, deriving from the photolysis of parent hydroperoxides, were suggested. © 1997 Elsevier Science S.A.

Keywords: Photoxidation; Terpenes; Hydroperoxidation

1. Introduction

Essential oils and their major components, terpenes, present a number of interesting properties largely valorized in very different domains [1] (perfumes [1a], drugs [1b], adhesives [1c], ...). Moreover these compounds have the precious label of 'natural products' which is particularly attractive in this end of century made exaggeratingly suscipicious towards chemicals coming from synthetic chemistry. From this point of view the appearance or the significant increase of anti-microbian properties of 'aged' terpenes or essential oils [2] is worth noting because of its potential applications. From a more fundamental aspect, the ageing of such unsaturated compounds has to be associated with the oxidation of olefins or unsaturated polymers and with the formation of intermediate hydroperoxides [3], if we consider, for example, their simple relationship with hydrogen peroxide whose anti-microbian properties are well known.

Recently, we were largely involved in the role of hydroperoxide in the ageing of dienic elastomers, such as EPDM based on 5-ethylidene-2-norbornene, and our experience of both the photochemical synthesis and the stability of the corresponding hydroperoxides incited us to perform the selective hydroperoxidation of typical terpenes present in pine oil and to measure the changes in their anti-microbian activity.

This first paper will report on the selective photochemical synthesis of α-, β-pinenes and limonene hydroperoxides and their characterization by using conventional iodometric titration, infrared, gas chromatographic/mass spectrometry (GC/MS) analysis as well as the derivatization of hydroperoxides into nitrates by nitric oxide treatment.

2. Experimental details

(+) and (−) stereoisomers of α-, β-pinenes and limonene were provided by Aldrich (purity ca. 97–99%) and used as received. Zinc oxide (ZnO–A from SMF Vieille Montagne) as well as anthracene or rose Bengal supported on polystyrene cross-linked by 2% of divinylbenzene (Fluka) were used as catalysts for hydroperoxidations. Solvents were toluene or acetonitrile (Aldrich).

Reactions were performed in an elliptical device containing both a source and a borosilicate reactor at each focal axis [4].

In the case of ZnO-photocatalyzed oxidation, the source was a fluorescent lamp (Philips TLD 15 w) emitting between 300 and 400 nm (ZnO absorbs radiations below 405 nm);

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the reactor was cooled by a water double-envelop and the suspension was stirred vigorously magnetically in the presence of oxygen bubbling [1] (15 min, twice a day). At the end of the reaction (typically few days) zinc oxide was carefully evacuated by decantation and centrifugation (5 min at 2500 rpm).

In the case of anthracene and rose Bengal photosensitized oxidation, sources were mercury lamps emitting respectively at $\lambda = 365 \pm 5$ nm (Mazda MAW 125) and at $\lambda > 300$ nm [2] (Mazda MA 400). Anthracene and rose Bengal absorb below 365 nm and at 550 nm respectively. The reactor for anthracene/365 nm oxidation was an open borosilicate tube equipped with a condenser; oxygen was gently bubbling during exposure ensuring both stirring and oxygenation of the toluene solution.

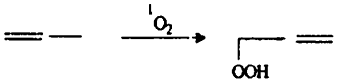
Analytical measurements were performed by infrared spectroscopy (Impact 400 Nicolet spectrometer, Omnic software) and by GC/MS (column: Cpwax 52 CB, 25 m, 0.25 mm; mass spectrometer HP 5 970 300). Hydroperoxides were evaluated by iodometry [5] and by nitric oxide derivatization [6]. This last technique, usually applied to polymer films is based on the quantitative conversion of hydroperoxides and alcohols (overlapping in the IR spectrum) respectively into corresponding nitrates and nitrites (having very different and very intense bands in IR spectroscopy).

$$\mathrm{ROOH} \xrightarrow{\mathrm{NO}} \mathrm{RONO_2}\ (1640,\ 1275-1300,\ 860\ \mathrm{cm^{-1}})$$

$$\mathrm{ROH} \xrightarrow{\mathrm{NO}} \mathrm{RONO}\ (1640,\ 760-780\ \mathrm{cm^{-1}})$$

3. Results and discussion

The synthesis of hydroperoxide can be performed by chemical and photochemical methods. Chemical methods such as nucleophilic substitutions of alcohols or brominated compounds were recently tested in our group on low molecular weight alcohols or polymers containing alcohol groups (polyvinyl alcohol, co(ethylene-vinyl alcohol)) as well as on brominated polyoctene [7]. The conversion into hydroperoxide was very low with a number of by-products; then careful purifications by chemical or chromatography methods were compulsory. Other methods such as the direct reaction of concentrated hydrogen peroxide [8] or the use of borane intermediates [9,10] are not expected to be much better. By photochemical methods a significant increase of the conversion (up to 40%) as well as the drastic reduction of by-products can be expected, especially by generating singlet oxygen with wavelengths sufficiently high to avoid the photochemical decomposition of hydroperoxides i.e. at $\lambda \geq 365$ nm.



This method is specific for unsaturated compounds and appears to be well adapted to terpenic substrates [11–17]; unfortunately most of the published work concerns analysis after reduction of hydroperoxides into corresponding alcohols. Another possible photochemical route is the use of photocatalysts, such as zinc oxide, titanium dioxide, ..., which, by excitation at wavelengths shorter than 380–400 nm, generate a number of active forms of oxygen ($^1O_2$ (Δg), O, $^{\cdot}$OH, $^{\cdot}$OOH...) capable of oxidizing any substrate. The filter effect of the pigment can induce a protection of photounstable oxidized products such as hydroperoxides or ketones and then makes possible a certain accumulation of hydroperoxide groups.

3.1. Zinc oxide-photocatalyzed oxidation of terpenes

The oxidation can be followed by FTIR spectroscopy and hydroperoxide titration. Spectra (differences after − before irradiation) are seen in Fig. 1(a) and 1(b) for α-pinene, they are characterized by the appearance of (i) two weak bands in the hydroxyl region assignable to alcohols (3580 cm^{-1}) and hydroperoxides (3491 cm^{-1}), and (ii) a strong symmetric band in the carbonyl region corresponding probably to ketonic groups. Carboxylic acids expected near 1550 cm^{-1} (zinc carboxylate) are not present, probably because of a good photochemical protection of ketones by the filter effect of zinc oxide [20]. Shoulders at 1730–1740 cm^{-1} cannot be definitely assigned, however, as we will see below, the presence of some aldehydic compound such as myrtenal can be expected. The unsaturation band of α-pinene seen initially at 1640 cm^{-1} is shifted towards 1627 cm^{-1} because of the formation of oxidized groups (OOH, OH, CO, ...) in the α position. Iodometric titration (Fig. 1(c)) shows that hydroperoxides do not accumulate and reach a plateau value corresponding to a 15% conversion for β-pinene. This plateau value results from an equilibrium between the formation and the decomposition of hydroperoxide both being photocatalyzed. Such a photocatalyzed decomposition of hydroperoxide was already reported in the case of terbutylhydroperoxide and polypropylene hydroperoxides [18].

Then the ZnO photocatalyzed oxidation is not a 'clean' route for the production of terpene hydroperoxides as ketones (major), alcohols and aldehydes are formed simultaneously [19]. However, the amounts of hydroperoxide available are sufficient to contemplate an eventual extraction by physical or chemical methods [3].

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[1] The same reactor was used for oxidation in the presence of a rose Bengal suspension.

[2] In few cases, radiations over 300 nm were filtered with a chemical filter ($CuCl_2$, 160 g l^{-1}/$CaCl_2$, 270 g l^{-1}/HCl/M, 1 ml) selecting radiations between 475 and 650 nm. Few tests were performed with a sodium lamp at $\lambda = 589$ nm (Mazda SIO, 18 W).

[3] See the second paper of this series; F. Chiron et al. in this journal.

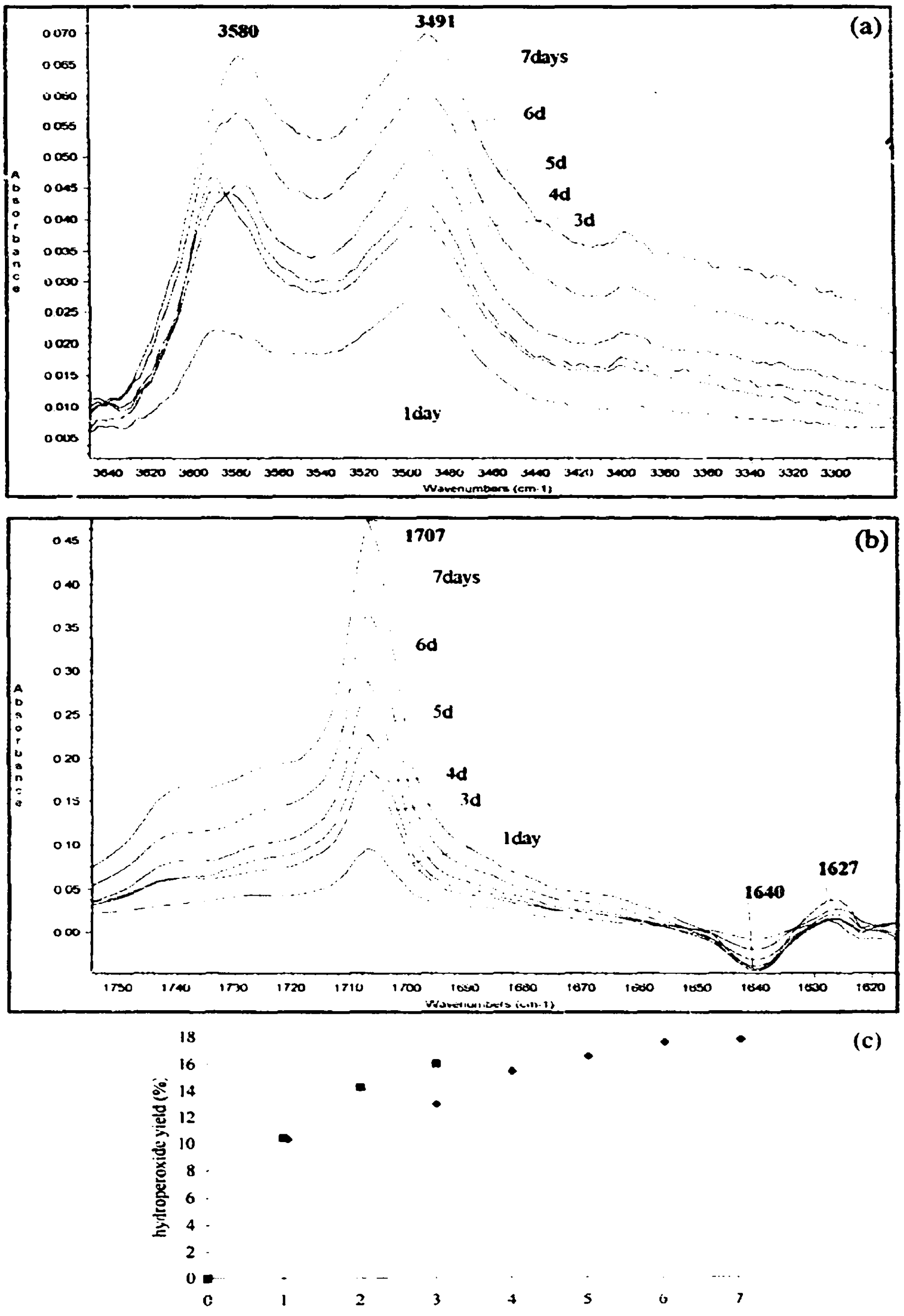
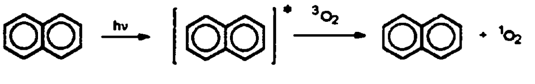


Fig. 1. IR ((a), (b)) and hydroperoxide content (c) changes upon the ZnO photocatalyzed oxidation of β-pinene.

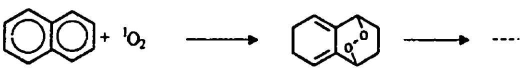
3.2. *Singlet oxygen oxidation of terpenes*

3.2.1. *Photosensitization by anthracene*

Anthracene was recently extensively used to perform the singlet oxygen oxidation of 5-ethylidene-2-norbornene residues present in the terpolymer ethylene/propylene/diene monomer (EPDM) [20]. This sensitizer was particularly useful as it was easily (i) introduced in the polymer before irradiation, and (ii) removed, together with its oxidation products, at the end of the reaction.



Indeed, an important secondary reaction, particularly at the solid state, is the formation of anthracene endoperoxide. This reaction is less important in dilute solutions of anthracene.



IR spectra in Fig. 2 show the changes in hydroxyl and carbonyl regions: the reaction is characterized by a selective production of hydroperoxides (3495 cm^{-1}) during the first 10 h of exposure. For longer irradiation times, small bands corresponding to alcohols (3570 cm^{-1}) or the carbonyl group (1707 cm^{-1}) can be observed. This phenomenon has to be correlated with the loss of anthracene (completely oxidized into anthracene endoperoxide in approximately 24 h). We showed in a previous study [20] that the production of hydroperoxide can be reactivated by the addition of new amounts of anthracene.

Terpene hydroperoxides (and eventual terpene alcohols) can be characterized by reaction with nitric oxide (see Fig. 3). In spite of the difficulty of eliminating correctly the sol-

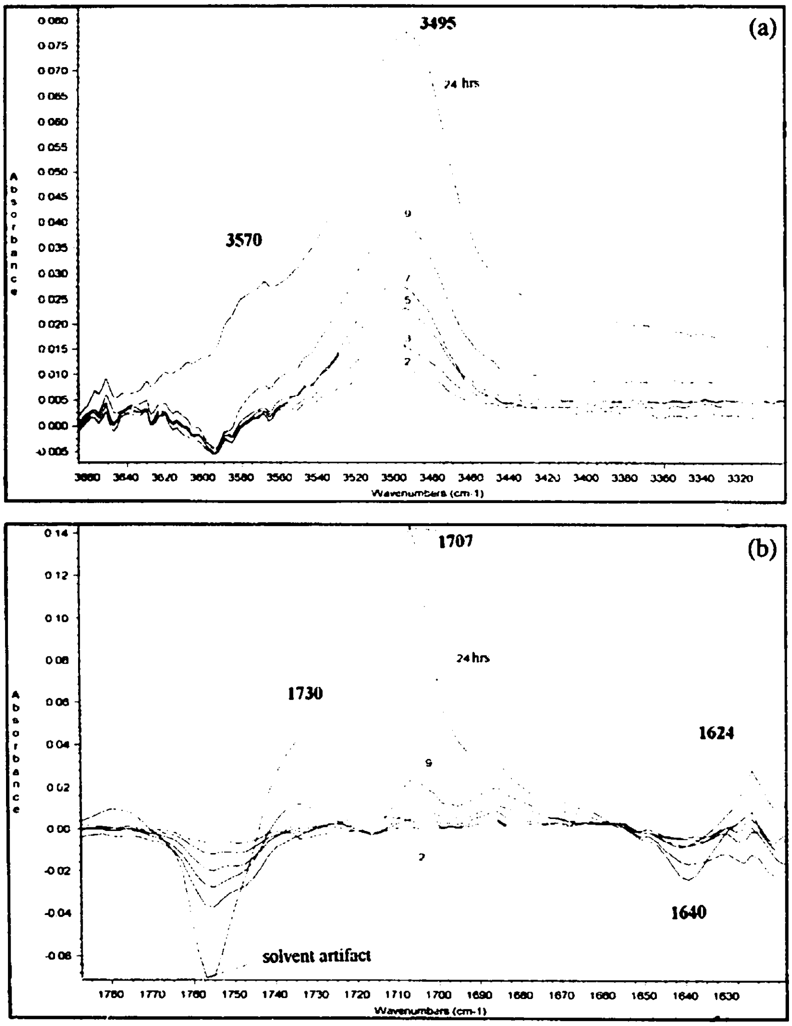


Fig. 2. IR changes upon the anthracene photosensitized oxidation of β-pinene.

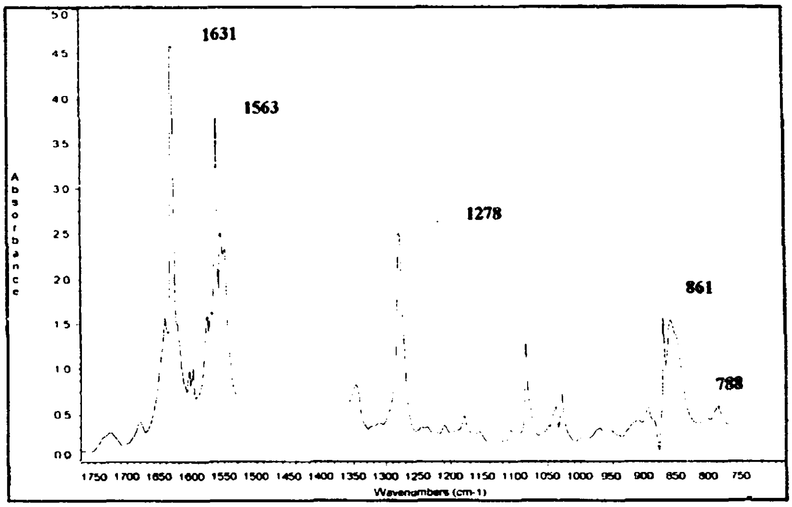
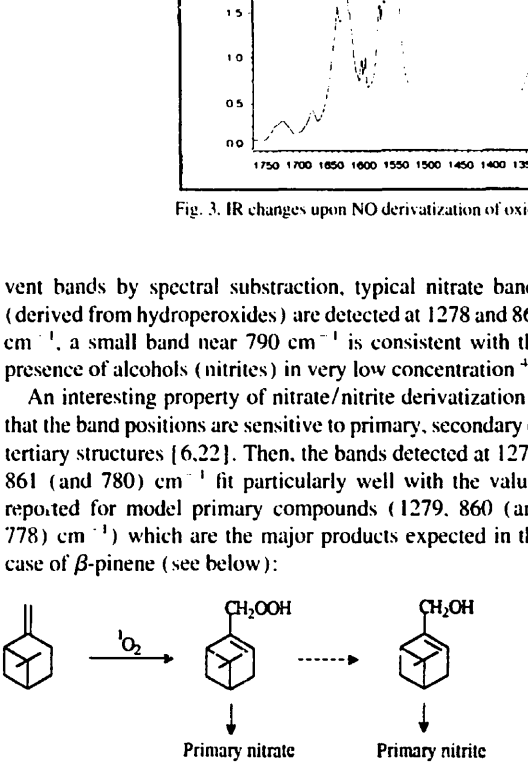


Fig. 3. IR changes upon NO derivatization of oxidized β-pinene (sensitizer, anthracene: exposure time, 17 h).

vent bands by spectral substraction, typical nitrate bands (derived from hydroperoxides) are detected at 1278 and 861 cm⁻¹, a small band near 790 cm⁻¹ is consistent with the presence of alcohols (nitrites) in very low concentration [4].

An interesting property of nitrate/nitrite derivatization is that the band positions are sensitive to primary, secondary or tertiary structures [6,22]. Then, the bands detected at 1278, 861 (and 780) cm⁻¹ fit particularly well with the values reported for model primary compounds (1279, 860 (and 778) cm⁻¹) which are the major products expected in the case of β-pinene (see below):



By using conventional absorption coefficients for hydroperoxides ($\epsilon_{3495}=70$ mol⁻¹ l cm⁻¹) and nitrates ($\epsilon_{1278}=$ 1210 mol⁻¹ l cm⁻¹) [25] it is possible to evaluate the hydroperoxide content and to compare it with iodometric titration. Results are reported on Table 1 for different experimental conditions.

The iodometric and the direct IR titration at 3495 cm⁻¹ are pretty closed while the IR titration of the nitrate derivative is undervalued probably because significant changes for the absorption coefficient value in toluene. The increase of both the substrate and the sensitizer concentration results in an increase of the amount of hydroperoxide however the conversion yield does not change a lot. The evolution of the conversion yield of β-pinene hydroperoxides vs. time is reported on Fig. 4. The formation rate of hydroperoxide is linear during the first stages of the reaction and decrease after 15 h, i.e. when anthracene is oxidized into anthracene peroxide. The conversion was found to be better in the case of α-pinene (0.32 instead of 0.16) probably because both the

Table 1
Hydroperoxide production along the anthracene-photosensitized oxidation of β-pinene (exposure, 17 h)

β-Pinene (10⁻² mol l⁻¹)	Anthracene (10⁻² mol l⁻¹)	Hydroperoxide (10⁻² mol l⁻¹)		
		Iodometric	–OOH at 3495 cm⁻¹	–ONO₂ at 1278 cm⁻¹
7.35	0.1	1.1 (0.16) [a]	1.2	0.8
7.35	1	1.4 (0.18) [a]	1.3	1.0
73.5	0.1	6.9 (0.09) [a]	6.6	3.5
73.5	1	10 (0.11) [a]	8	3.6

[a] Conversion yield.

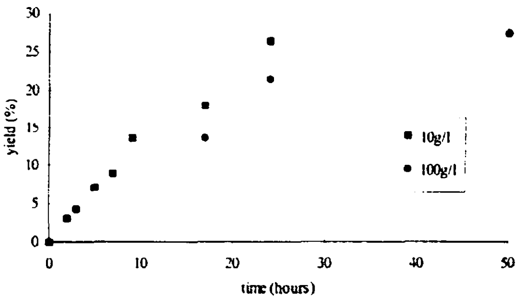


Fig. 4. Hydroperoxide changes upon anthracene photosensitized oxidation of β-pinene (■, 10 g l⁻¹; 124●, 100 g l⁻¹).

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[4] A very intense band is also seen at 1630–1640 cm⁻¹ however this band is not specific (deriving from both nitrates and nitrites).

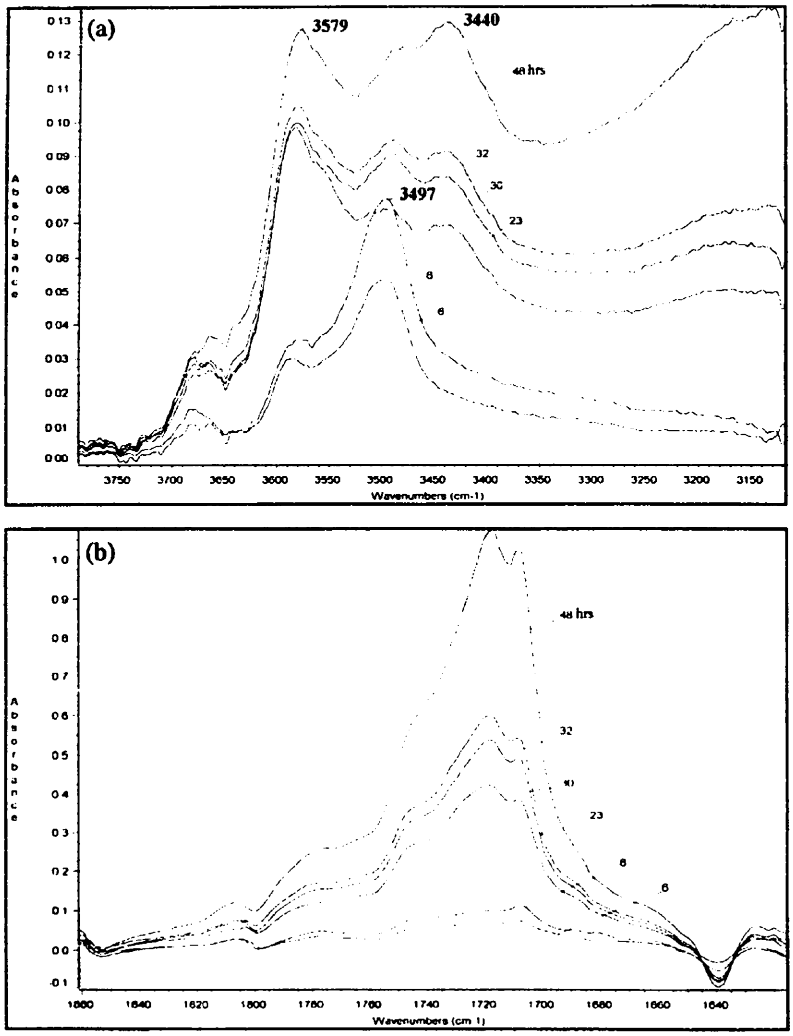
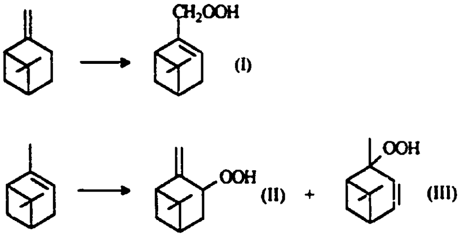


Fig. 5. IR changes upon the rose Bengal photosensitized oxidation of β-pinene (irradiation at λ ≥ 300 nm).

higher stability of the expected hydroperoxides and the best reactivity of substituted olefins.



3.2.2. Photosensitization by rose Bengal

Rose Bengal supported on cross-linked polystyrene is particularly adapted to the case of the hydroperoxidation of low molecular weight compounds in toluene solution as it can be easily eliminated at the end of the reaction by centrifugation or filtration. However, similar to anthracene, rose Bengal is slowly oxidized along the reaction and turns yellow after 8–10 h at λ > 300 nm.

The shapes of the IR spectra (Fig. 5) again show a selective hydroperoxidation (a single band at 3497 cm^{-1}) at the beginning of the reaction (the first 8–10 h) and the further development of alcoholic and carbonyl groups. The influence of experimental conditions on the production of hydroperoxide is reported in Table 2 for β-pinene.

Here again, the increase of the concentration in substrate and sensitizer increase slightly the amount of hydroperoxide but not the yield of the reaction (optimum for [A] = 0.1 mol l^{-1}; [BR] = 3 g l^{-1}). A second addition of rose Bengal (old rose Bengal was eliminated from the suspension) allows a significant increase of the conversion; however, the produc-

Table 2
Hydroperoxide production by rose Bengal photosensitized oxidation of β-pinene

(−) β-Pinene (mol l^{-1})	Rose Bengal (g l^{-1})	Exposure time (h)	Hydroperoxide	
			10^{-2} mol l^{-1}	Yield (%)
1	6.67	8	6.6	0.066
1	3	8	9.3	0.093
0.1	3 + 3	8 + 8	4.0	0.40
0.1	3	8	2.7	0.27
0.1	3	6	6.3	0.63 [a]
0.1	1	7	1.2	0.12

[a] Reaction performed in acetonitrile instead of toluene.

tion of alcohol and ketone was also increased. The use of a more polar solvent (acetonitrile) increases the production of hydroperoxide; however, the OH region of the IR spectrum becomes more complex because of possible hydrogen bond associations between hydroperoxide and nitrile groups (early bands at 3624, 3537 and 3389 cm^{-1}).

All three terpenes gave similar results, however limonene hydroperoxidized more rapidly (see Fig. 6). For each terpene the same result was obtained for both stereoisomers.

The reaction can be improved by eliminating short wavelengths which are responsible of the decomposition of both sensitizer and hydroperoxide.

A sodium lamp (λ = 589 nm) and a chemical green filter (transparent between 475 and 650 nm) associated with the

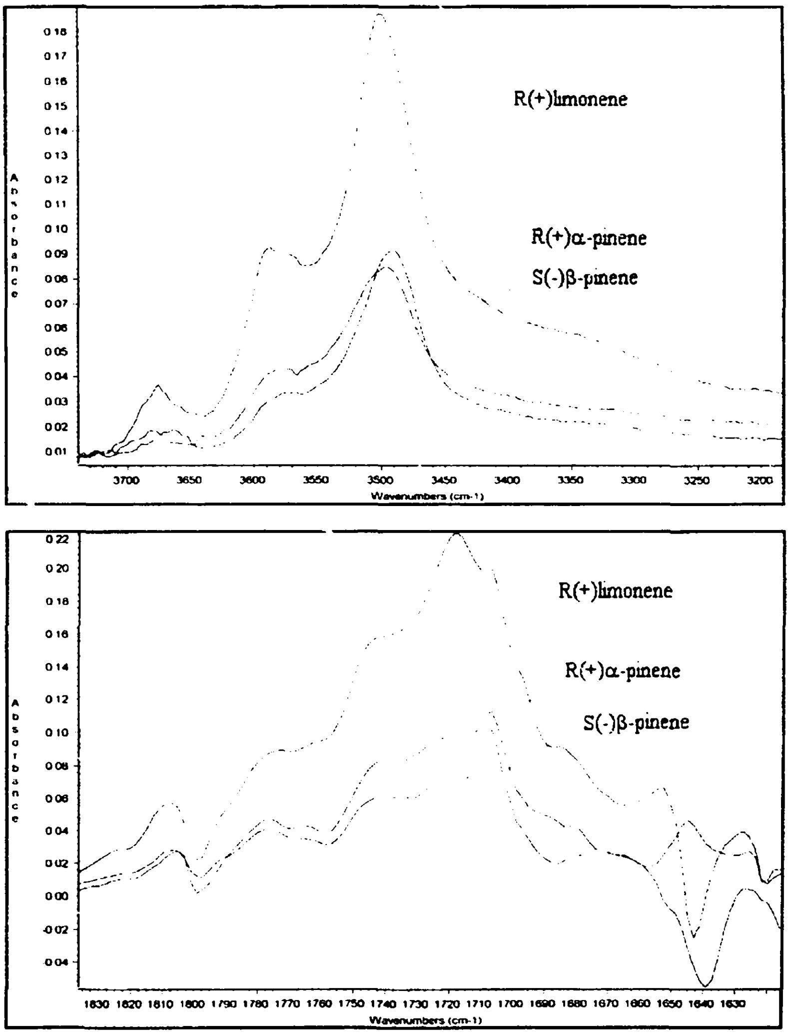


Fig. 6. Comparison of IR spectra of oxidized R(+) α-pinene, S(−) β-pinene and R(+) limonene (sensitizer, rose Bengal; exposure time, 8 h).

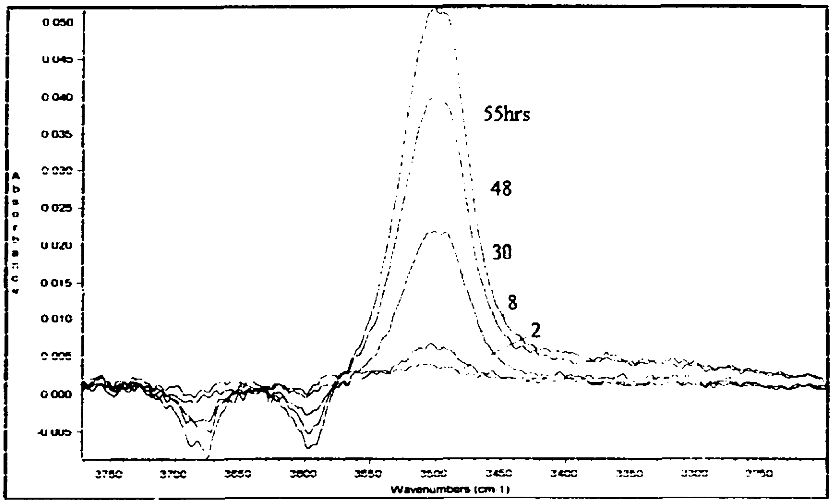
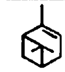
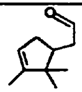
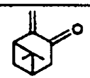
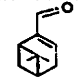
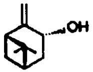
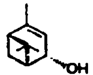
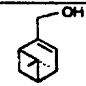
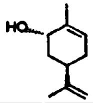


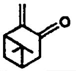
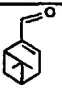
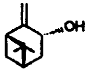
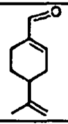
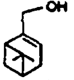
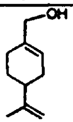
Fig. 7. IR changes (hydroperoxide) upon the rose Bengal photosensitized oxidation of β-pinene (irradiation with sodium lamp, λ = 589 nm).

Table 3
Secondary products from the rose Bengal sensitized oxidation of (+) and (−) α-pinenes

		substrate	
compound	structure*	(+)α-pinene	(-)α-pinene
α-pinene		59.2	39.4
epoxy-α-pinene		4.0	1.7
campholenal		trace	trace
pinocarvone		12.8	28.1
myrtenal		3.4	3.1
transpinocarveol		14.3	22.1
transverbenol		2.2	trace
myrtenol		1.9	2.4
transcarveol		2.3	3.3

* represented structure corresponds to the (+) substrate.

Table 4
Secondary products from the rose Bengal sensitized oxidation of (+) and (−) β-pinenes

		substrate	
compound	structure	(+)β-pinene	(-)β-pinene
β-pinene		84.8	92.5
pinocarvone		0.3	trace
nopinone		trace	trace
myrtenal		9.8	3.6
transpinocarveol		0.9	0.7
perillic aldehyde		0.6	0.4
myrtenol		3.2	2.5
perillic alcohol		0.4	0.3

* represented structure corresponds to the (+) substrate.

source emitting at $\lambda > 300$ nm were tested (rose Bengal absorbs at 550 nm). Fig. 7 shows the evolution of the hydroperoxide band by using the sodium lamp; the reaction is very clean but very long irradiation times were necessary because of both the low lamp intensity and the low absorption of the sensitizer at 589 nm.

Secondary products were analyzed by GC/MS for all terpenes. Reactions were stopped at a constant level of hydroperoxide (2.6×10^{-2} mol l^{-1}; yield, 0.26) [5]. For better identification, solutions were concentrated three times before analysis. Identifications were made with reference to MS spectra [23,24] and (or) by co-injection of authentic products.

Results are reported in Tables 3–5 for α, β-pinenes and limonenes respectively.

The structures and the contributions of hydroperoxides can be deduced from the alcohol GC/MS analysis [12,17]. Results are as shown in Table 6.

The primary hydroperoxide expected for β-pinenes is effectively the major observation; however for α-pinenes, only the secondary hydroperoxide seems to be formed as the tertiary alcohol was not found among the GC/MS products. Conversely, both tertiary ($\approx 60\%$) and secondary hydroperoxides are produced in the case of limonene.

Most of the secondary products observed during the hydroperoxidation of the three terpenes can be interpreted as deriving from the decomposition (mainly photochemical) of the hydroperoxides formed by singlet oxygen oxidation (ene reaction) or by auto-oxidation (hydroperoxidation in the α-position of the double bond). The possible mechanisms for the formation of the main by-products are reported in Fig. 8(a), 8(b) and 8(c), respectively, of the oxidation of α, β-pinenes and limonenes.

4. Conclusion

Terpene hydroperoxides can be easily synthesized by photochemical oxidation of parent terpenes. Photocatalysts, such as zinc oxide, or sensitizers, such as anthracene or rose Bengal, allow a conversion between 15 and 40%.

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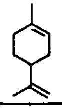
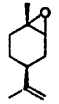
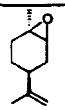
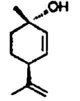
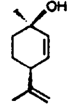
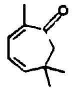
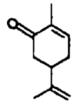
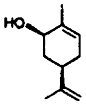
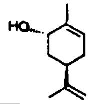
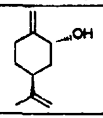
[5] Hydroperoxide were not detected with our analytical conditions.

Table 5
Secondary products from the rose Bengal sensitized oxidation of (+) and (−) limonenes

		substrate	
compound	structure	(+)limonene	(-)limonene
limonène		91.6	90.3
1,2-epoxy-cis-limonene		0.9	1.0
1,2-epoxy-trans-limonene		0.5	0.7
cis-p-mentha-2,8-dien-1-ol		2.7	3.4
trans-p-mentha-2,8-dien-1-ol		0.7	0.8
eucarvone		trace	trace
carvone		trace	trace
cis-carveol		1.2	1.2
trans-carveol		0.9	0.8
trans-p-mentha-1(7),8-dien-2-ol		1.6	1.7

* represented structure corresponds to the (+) substrate.

In the presence of zinc oxide, hydroperoxides are always obtained together with alcohols and ketonic/aldehydic groups; the reason for this is the competitive photocatalytic decomposition of hydroperoxides and the multiple ways for peroxide radical decomposition [21].

$$ZnO \xrightarrow{h\nu/O_2} \underset{\text{(Active Species of Oxygen (ASO))}}{O^*, {}^{\cdot}OH, {}^{\cdot}OOH, {}^1O_2(\Delta g)\ldots}$$

$$RH \xrightarrow{ASO} R^{\cdot} \xrightarrow{O_2} ROO^{\cdot} \xrightarrow[\text{solvent}]{RH} ROOH + \text{alcohols, carbonyls}$$

$$ROOH \xrightarrow{ASO} ROO^{\cdot} \rightarrow \text{alcohols, carbonyls, } \ldots$$

The formation of hydroperoxides is only possible by singlet oxygen oxidation. Anthracene and rose Bengal are effi-

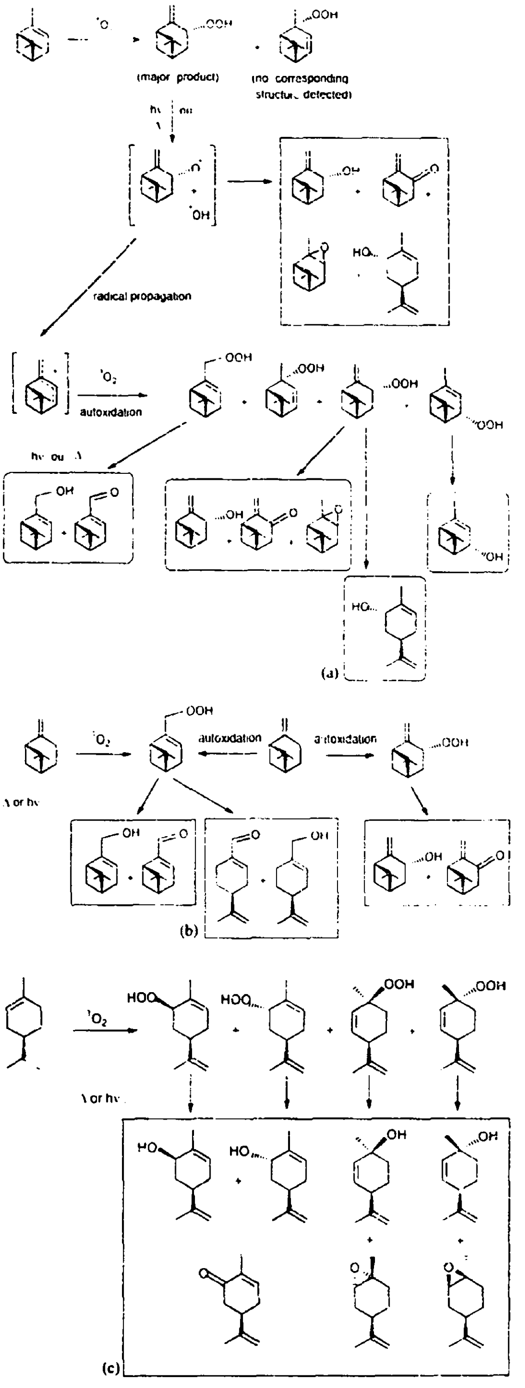
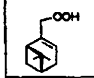
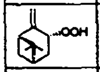
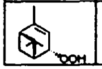


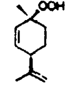
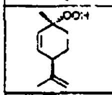
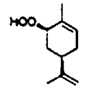
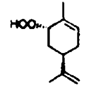
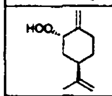
Fig. 8. Suggested mechanisms for the photosensitized oxidation of α-pinene (a), β-pinene (b) and limonene (c).

cient sensitizers; however, their own decomposition has to be slowed down by reducing their concentration and by using wavelengths as high as possible so that the hydroperoxide cannot absorb. The structure of hydroperoxides can be obtained by nitric oxide derivatization or more certainly by studying the structure of the resulting alcohols by GC/MS.

Table 6
Structure and content of hydroperoxides derived from the sensitized oxidation of α, β-pinenes [6]a and limonenes [6]b (results deduced from GC/MS analysis of corresponding alcohols)

[6a]	(+)α-pinene	(-)α-pinene	(+)β-pinene	(-)β-pinene
	13	9	92	91
	82	91	8	9
	5	trace	-	-

* represented structure corresponds to the (+) substrate.

[6b]	(+)limonene	(-)limonene
	19	19
	38	43
	14	12
	10	8
	19	18

* represented structure corresponds to the (+) substrate.

Most of the hydroperoxides expected from the ene reaction on the three terpenes has been retrieved, excepting the tertiary hydroperoxide deriving from the hydroperoxidation of α-pinenes (absence of the corresponding alcohol).

Secondary products appearing for long irradiation times (typically > 9–10 h) has been identified by GC/MS analysis; most of them derived from the photolysis of the parent hydroperoxides.

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