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Fluorescence emission and photooxidation studies with 5,6- and 6,7-benzocoumarins and a 5,6-benzochromone under direct and concentrated sun light

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Abstract

4-Methyl-8-hydroxy-benzo(6,7)coumarin, I, 4-methyl-6-hydroxy-benzo(5,6)coumarin, II, and 2-methyl-6-hydroxy-benzo(5,6)chromone, III, have shown similar absorption and fluorescence emission spectra. Fluorescence emission quantum yields for I and III are found to be very low, $\phi_f = 0.02$, but 4-methyl-6-hydroxy-benzo(5,6)coumarin, II, has a eight-fold higher fluorescence quantum yield of the other two specie, in acetonitrile solution, $\phi_f = 0.16$. Quenching of anthracene fluorescence emission by I, II and III are found to give k_q values of 1.0×10^7–$1.2 \times 10^9\ M^{-1}\ s^{-1}$. Benzo(5,6)coumarin, II, which gives the most intense fluorescence also presents the highest quenching rate, $k_q = 1.2 \times 10^9\ M^{-1}\ s^{-1}$. Experimentally determined k_q values are seen to correlate well with the free energy of electron transfer (ΔG_{ET}) which are calculated to be in the range of −8.0 to −9.4 kcal/mol, where benzo(5,6)coumarin, II, gives the lowest free energy of electron transfer $\Delta G_{ET} = -9.4$ kcal/mol. These results indicate that I–III behave as electron acceptor moieties toward a condensed aromatic ring, anthracene. The Stokes shift values of 88–105 nm and broad fluorescence emission bands respect to absorption–excitation bands, indicates a molecular structure change in the excited states of I–III. Fluorescence lifetimes of 0.1–0.9 ns in I–III, singlet oxygen quantum yields of 0.15 and 0.40 for I and II, respectively, may be taken as evidence of singlet–triplet intersystem crossings. The photooxidation products of α-terpinene, sensitised by II, under direct and concentrated sun light conditions that are mainly *p*-cymene and ascaridole. In accordance with literature data on coumarin derivatives, benzocoumarins also seem to produce singlet oxygen and beside singlet oxygen, in addition super oxide anion radical production appear to be dominant especially under concentrated sun light. Under direct sun light conditions ascaridole is the major product. Some by-products of α-terpinene photooxidation are also determined at GC–MS analysis. Those by-products are assumed to be generated from ascaridole decomposition.

Keywords: Fluorescence lifetime; Quenching of fluorescence emission; Benzocoumarin; Benzochromone; α-Terpinene; Photooxidation

1. Introduction

Coumarins and chromones are well known pigments and have been studied widely for their luminescent properties and applications, i.e. laser dyes, optical brighteners [1]. In comparison, benzocoumarins and benzochromones are less studied for their fluorescence data and photosensitive properties. Recently, the application of benzocoumarins as non-linear optical devices [2] and fluorescent whiteners [3] have been reported. Fluorescence emission of a bromomethyl derivative of benzocoumarin was employed for HPLC–fluorometric analysis of marine organisms [4]. Two bioactive benzocoumarins have been isolated from Vismia guianensis [5] and a benzochromone has been isolated from the roots of Sophora exigua [6]. 5,6-Benzocoumarin-5-uracil is used for a bio-medical treatment [7]. Benzochromone and benzocoumarin derivatives are under focus because of their interaction with HIV reverse transcriptase also [8]. All of these observations hint that there is a cause of biological functions of benzocoumarins, benzochromones in nature. Liu et al. reports the antioxidative effect of 4-methylcoumarin and 7-hydroxy-4-methylcoumarin at photosensitized peroxidation of human low-density lipoprotein [9]. There are no reports in literature on photooxidation processes and mechanisms of any benzocoumarins and benzochromones. On the other hand, a microbiological study reports that 6,7-benzocoumarin present in an enzyme degrades the condensed aromatic structure of

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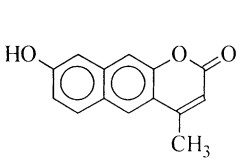
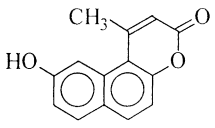
anthracene by an oxidation process [10]. In agreement with, another aromatic hydrocarbon, fluorine is found to be oxygenated by Pseudomonas microorganism, where 8-hydroxy-3,4-benzocoumarin was present [11]. All these results point that benzocoumarins and benzochromones may be the effective photocatalysts at oxidative degradations under natural conditions.

Photooxidation of dyes and electron-rich substrates such as alkenes, dienes and amines in aerated organic solutions by dye sensitisation of molecular oxygen are regarded as ubiquitous [12,13]. Recently, photooxidation of trihydroxybenzenes, 3-strylthiophene, sulfur compounds, α-pinene and poly(para-xylylene) by dye sensitisation took their place in literature [14–18]. Chen et al. performed the photooxidation of α-terpinene by a perylenediimide derivative and their results indicated a novel photooxidation that proceeds by an initial electron transfer quenching of the dye singlet by diene, followed by a reaction of the exciplex with oxygen [19].

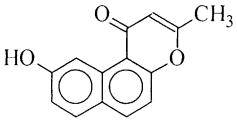
We now report the fluorescence emission data on linear and non-linear benzocoumarins and a non-linear benzochromone and photooxidation of α-terpinene sensitised by II. Quenching of fluorescence emission of an aromatic donor molecule, anthracene, displayed the magnitude of photo energy transfer to acceptor benzocoumarins and benzochromone molecules.



4-Methyl-8-hydroxy-benzo(6,7)coumarin, I



4-Methyl-6-hydroxy-benzo(5,6)coumarin, II



2-Methyl-6-hydroxy-benzo(5,6)chromone, III

2. Experimental details

2.1. Reagents

Benzocoumarins and benzochromone were synthesized as reported [20]. Solvents, acetonitrile and cyclohexane, were supplied from Aldrich in HPLC grade, used without any treatment. Fluorescence quantum yields were calculated in reference to fluorescence emission of 9,10-diphenyl anthracene (DPA) at $\lambda_{exc} = 345$ nm in cyclohexane solution, $\phi_f = 0.90$ [21]. DPA was supplied from Aldrich and anthracene from Aldrich in GOLD LABEL grade. Phenazine that is taken as a reference at singlet oxygen quantum yield (ϕ_Δ) determinations has a value of $\phi_\Delta = 0.84$ [22] at $\lambda_{exc} = 354$ nm in $CHCl_3$. Tetrabutylammonium hexafluorophospate ([TBA][PF_6]) was used as the electrolyte in cyclic voltametric measurements and was supplied from Aldrich.

2.2. Instrumentation

Spectroscopic measurements were done with Jasko V-530 and HP 8453 UV-Vis spectrophotometers and PTI-QM1 and Spex-Fluorolog fluorescence spectrophotometers. ϕ_Δ determinations were done with a Quanta-Ray DCR-2 Nd:YAG laser associated with 0.25 m Jarrell-Ash Monochrometer for the isolation of 1270 nm emission and Schott KG-3 filter on exit port. CV-27 cyclic voltammograph with a Ag/AgCl reference electrode was used for the determination of redox potentials. Concentrated sun light experiments were performed with Fix Focus FF 3,5-HTC GmbH (Germany) instrument with a reflective surface are of 2.66 m^2. The radiation intensity was determined by using Vilbert Loumart radiometers at 254 and 312 nm radiation wavelengths, and compared with the measured intensity of direct sunlight using the same radiometers. Direct sun light experiment was performed in ambient air. Aeration in photoreactor was accomplished by using a aquarium pump. GC–MS analysis were done using an HP 6890 instrument with a mass selective detector and HP-5MS phenyl methyl siloxane capillary column, at an initial oven temperature of 40 °C and maximum temperature of 280 °C.

2.3. Experiment conditions

Fluorescence quantum yields determined in reference to 9,10-diphenylanthracene and the index of refraction index differences in solvents were included at calculations. Anthracene was employed in fluorescence quenching studies with benzocoumarins and benzochromone. Quenching of fluorescence emission of anthracene was recorded by addition of benzocoumarins, I, II and benzochromone, III, (1.0–1.7) × 10^{-5} M, into the anthracene solution in acetonitrile and for both donor and acceptor the solvent was acetonitrile. In order to be sure that the quenching was not trivially associated with the competitive absorption by I–III, the concentrations of the quenchers were kept around 10^{-6} M which corresponds to absorption values between 0.03 and 0.05 at λ_{max}. All fluorescence emission spectra for fluorescence quantum yield measurements and fluorescence emission quenching were corrected.

In ϕ_Δ determinations, the solutions of I, II and phenazine were prepared at approximate absorptions of 0.4, 0.3, 0.2 to 0.1 for 355 nm absorption band in $CHCl_3$. Benzochromone, III, could not have been studied, because of low solubility in $CHCl_3$; maximum absorption was measured to be only 0.14.

In cyclic voltametric measurements, the blank cycle was performed with 100 mM [TBA][PF_6] in ACN and seen that it works between 1.35 and −1.55 V. Redox potentials of I–III, from reversible waves calculated as $[E_{p(ox)} + E_{p(red)}]/2$ (ACN solvent).

Photooxidation of α-terpinene was done by the sensitisation of II both under direct and concentrated sun light in a Pyrex photoreactor. The 0.1 M α-terpinene solution in acetonitrile was prepared and a few mg of II was added into the solution. Reaction was controlled by TLC method using a toluene:ethylacetate; 4:1 solvent mixture. When α-terpinene spot was disappeared, 10 ml of the solution was mixed with 10 ml 0.1 M Na_2SO_3 and stirred for 5 h. Extraction of the products to $CHCl_3$ phase and following dehydration with $CaCl_2$ were performed. Irradiation intensity was controlled although the process was determined between 135 and 150 sun. *p*-Cymene, ascaridole, 3-isopropyl-2-heptenal-6-on, 3,7-dimethyl-2-octenal-6-on and 6-methyl-2,5-dion-3-hepten were detected as photooxidation products via mass spectra by the observation of their characteristic molecular ions as below:

(A) *p*-Cymene, detection time 11.30–11.35 min. At *m*/*z* 134, the molecular ion (M^+) peak is observed. Two strong fragment ions were observed at *m*/*z* 119 and 91. A loss of 15 (–CH_3) and 43 (–$CH(CH_3)$) from 134 produce *m*/*z* 119 and 91, respectively. It is obvious that *m*/*z* 77 belongs to the benzene ring.

(B) Ascaridole, detection time 22.99–23.06 min. The molecular ion peak is observed at *m*/*z* 168. Three strong fragment ions were observed at *m*/*z* 125, 97 and 43. The *m*/*z* 43 has to be –$CH(CH_3)_2$ as *m*/*z* 125 corresponds to its cleavage. A loss of 71 (CH_2=CH_2 plus –$CH(CH_3)_2$) from 168 could produce *m*/*z* 97.

(C) 3-Isopropyl-2-heptenal-6-on, detection time 21.89 min the same with (B), molecular ion peak is observed at 168 (Fig. 1). Three strong fragment ions were at *m*/*z* 155, 127 and 109 which probably correspond to the

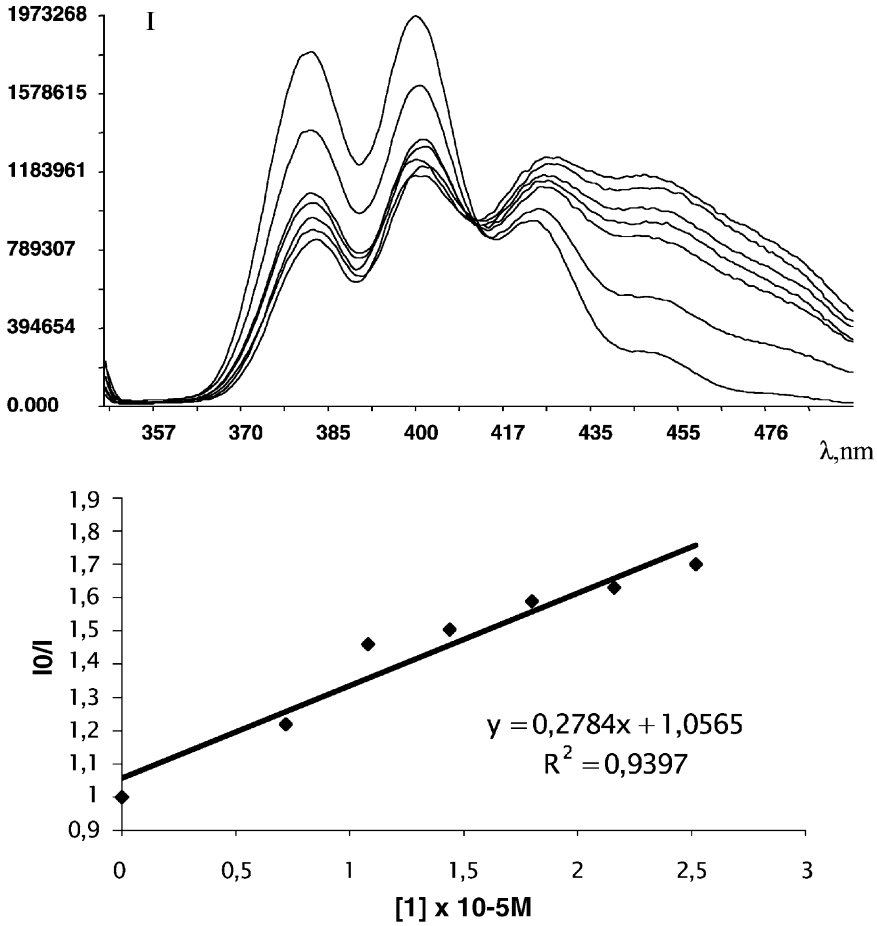


Fig. 1. Fluorescence quenching of anthracene (λ_{exc} = 339 nm) by 4-methyl-8-hydroxy-benzo(6,7)coumarin, I, in acetonitrile at quencher concentrations of (1.0–1.7) × 10^{-5} M and the Stern–Volmer plot.

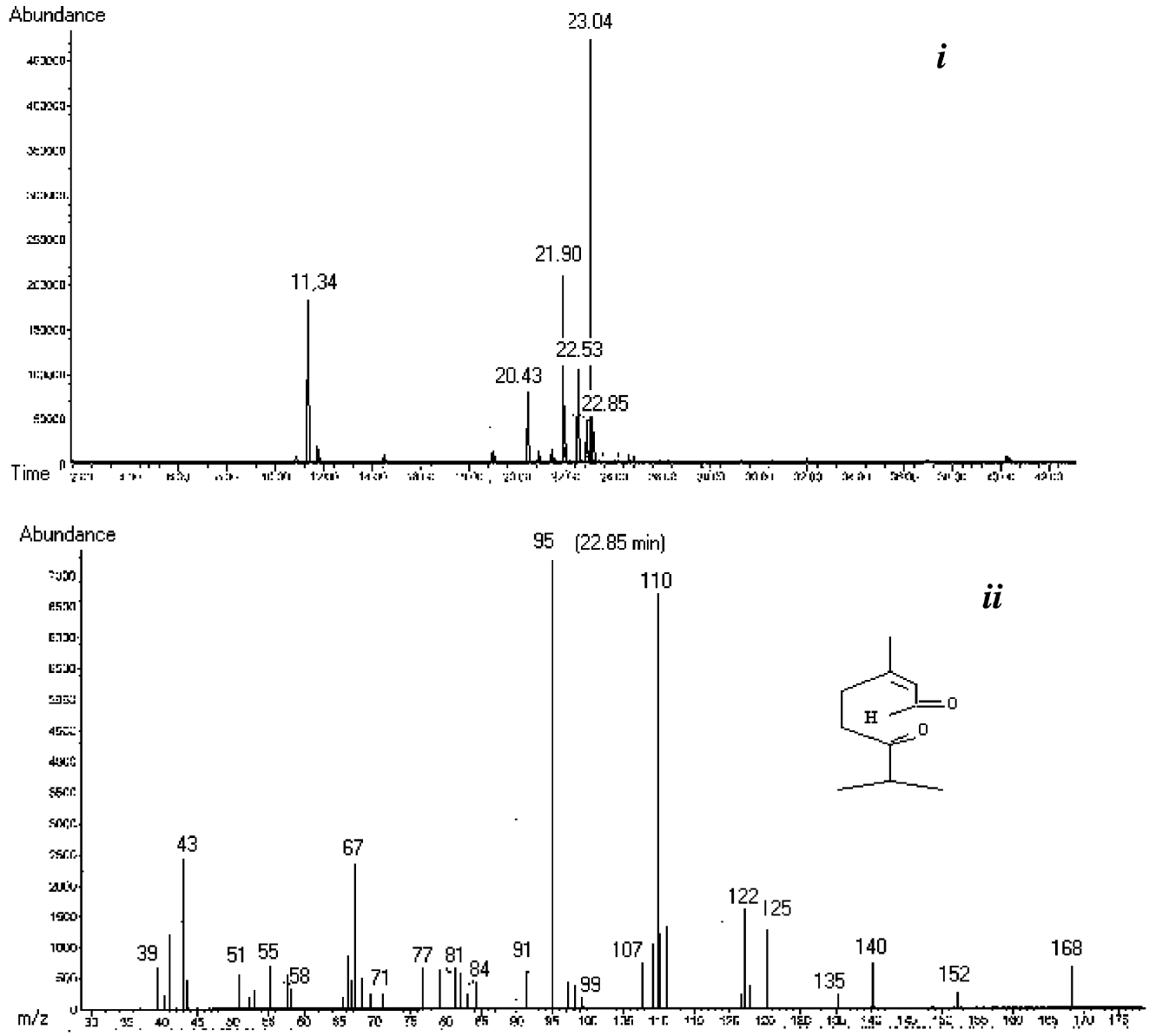


Fig. 2. Retention time vs. abundance for the direct sunlight experiment (i) and mass spectrum of 3,7-dimethyl-2-octenal-6-on (D) (ii).

$-CH_3$, $-C(CH_3)O$, $-C(CH_3)_2OH$ cleavages from *m/z* 168, respectively.

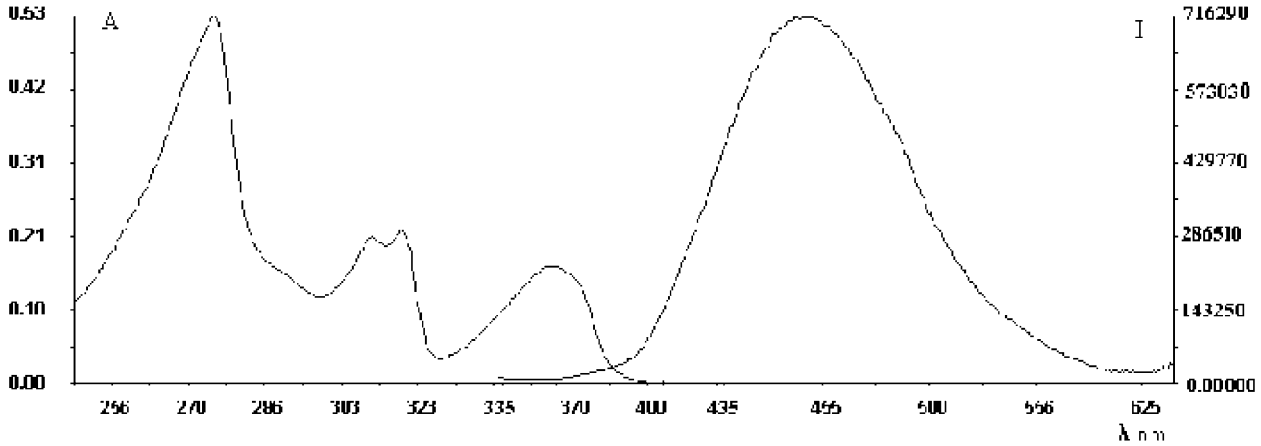
(D) 3,7-Dimethyl-2-octenal-6-on, detection time 22.85–22.89 min. Again the same with (B), molecular ion peak is observed at *m/z* 168 (Fig. 2). Different from (C) the strong fragment ions were at *m/z* 140, 125, 110 and 95. A loss of 28 (–CO) from 168 could produce *m/z* 140. A loss of 15 ($-CH_3$) from 140 will give *m/z* 125. With the loss of second 15 ($-CH_3$) *m/z* 110 is reached. And at last *m/z* 95 could be the loss of 73 ($-C(CH(CH_3)_2O)$) from *m/z* 168.

(E) 6-Methyl-2,5-dion-3-hepten, detection time 20.42 min. A base peak ion at *m/z* 140 (Fig. 2). Two fragment ions were observed at *m/z* 97 and 43. The loss of 43 ($-C(CH_3)O$) from 140 will produce *m/z* 97.

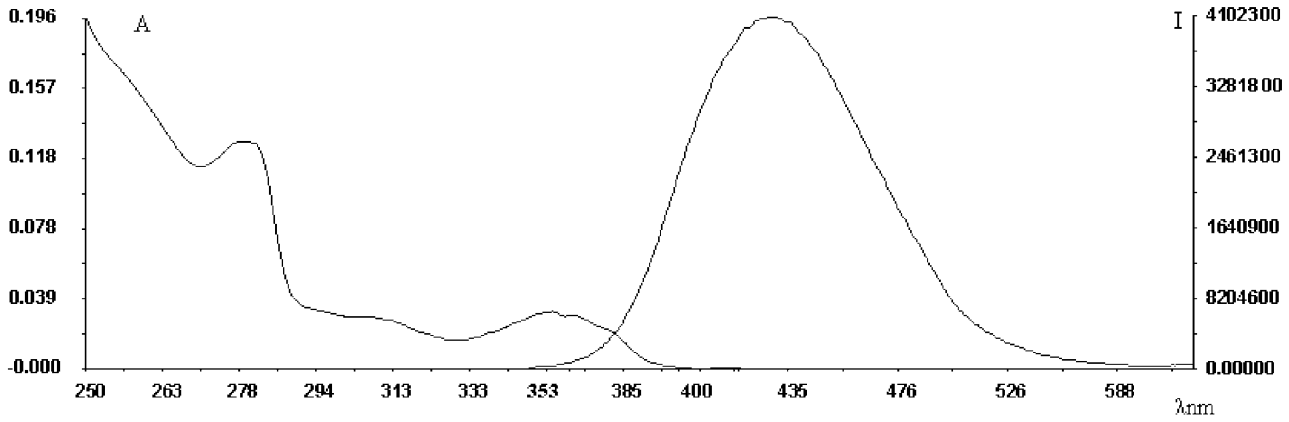
3. Results and discussions

3.1. UV-Vis, fluorescence emission and ϕ_Δ determination studies

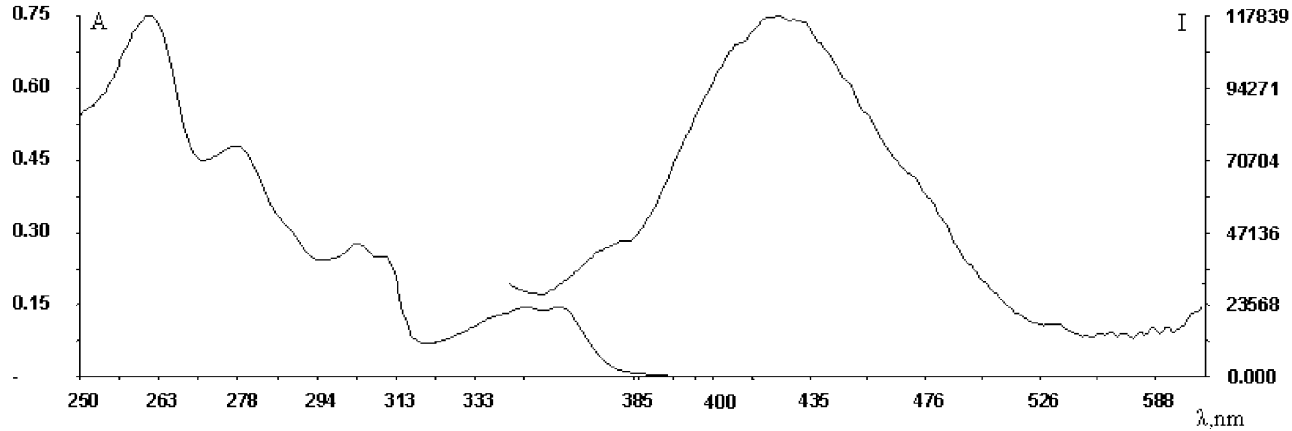
Coumarins are reported to have two band groups of UV absorptions at 270–280 and 310–350 nm, arising from π–π^* transitions [23]. Chromone derivatives seem to have similar absorption characteristics [24]. In accordance, 6,7-benzocoumarin, I, 5,6-benzocoumarin, II, and 5,6-benzochromone, III, show absorptions of two band groups at 274–287 and 322–347 nm regions (Fig. 3 and Table 1). The band at 322–347 nm is expected to be the result of overlap of π–π^* band with n–π^* band for these compounds. No notable UV absorption wavelength change



UV-Vis and fluorescence emission spectra of compound I.



UV-Vis and fluorescence emission spectra of compound II.



UV-Vis and fluorescence emission spectra of compound III.

Fig. 3. UV-Vis and fluorescence emission spectra of compounds I–III in acetonitrile solutions and $\lambda^{I}_{exc} = 342$, $\lambda^{II}_{exc} = 346$, $\lambda^{III}_{exc} = 336$ nm, respectively.

Table 1
The UV absorption, λ (nm), ε (mol^{-1} cm^{-1} l), fluorescence emission data, λ^f (nm) of studied compounds I, II and III in acetonitrile solutions

Compound	λ_{max}	ε_{max} ($\times 10^4$)	λ^f_{max}
I	232	8.14	
	277	2.32	
	287	2.57	
	343	2.05	450
II	240	11.2	
	280	2.70	
	332	2.80	
	347	2.50	429
III	235	5.75	
	274	4.03	
	266	4.45	
	322	2.30	
	336	2.30	430

from linear benzocoumarin, I, to non-linear benzocoumarin, II, is seen in Table 1. All three studied compounds, I-III are found to fluorescence with weak to moderate intensities at excitation of longest wavelength absorption. Fluorescence emissions at 430–450 nm suggest that benzocoumarin and benzochromone derivatives of I–III are expected to lase at 430–450 nm. Some coumarin derivatives are known as laser dyes at 440 nm [1].

The fluorescence emission bands of I–III are found not to be similar to the absorption and excitation bands, but broader in comparison to the absorption band (Fig. 3) and the excitation band (Fig. 4). A structural change in molecules I–III may have been taking place at the excited state. Fluorescence quantum yields calculated in reference to 9,10-diphenylanthracene, is seen to differ about eight-fold from $\phi_{f1} = 0.02$ in linear 6,7-benzocoumarin, I, and non-linear 5,6-benzochromone, III, to $\phi_{f1} = 0.16$ in non-linear 6,7-benzocoumarin, II (Table 2). Substitution on the hetero and benzene rings of coumarins has been reported to alter fluorescence emission strongly [1]. Unsubstituted coumarin fluoresces very weakly, $\phi_{f1} < 10^{-4}$ [23], but 7-diethylamino-4-methyl-coumarine is reported to fluoresce in high yield, $\phi_{f1} = 0.73$ [25]. Stokes shifts of benzocoumarins and benzochromone, measured from excitation and fluorescence spectra (Fig. 4), are in the range of 88–105 nm. Moderately high Stokes shift values may also suggest again that some structural change is present at the excited states of the compounds I–III.

Table 2
Singlet energies, E_s(kcal/mol), fluorescence quantum yields, ϕ_f, singlet oxygen quantum yields, ϕ_Δ, Stokes shifts, Δλ (nm), radiative lifetimes, τ_o(ns), fluorescence lifetimes, τ_f (ns) and fluorescence rate constants, k_f (10^7 s^{-1}), data of I, II and III in acetonitrile

Compound	λ_{abs}	E_s	ϕ_f	ϕ_Δ	Δλ	τ_o	τ_f	k_f
I	343	83.4	0.02	0.15	105	6.7	0.1	1.5
II	347	82.5	0.16	0.40	99	5.6	0.9	1.8
III	336	85.2	0.02		88	5.8	0.1	1.7

The radiative lifetimes, τ_o, in Table 2, were calculated by the formula: $\tau_o = 3.5 \times 10^8/\nu^2_{max}\ \epsilon_{max}\ \Delta\nu_{1/2}$, where ν_{max} is the wavenumber in cm^{-1}, ϵ_{max} the molar extinction coefficient at the selected absorption wavelength, and $\Delta\nu_{1/2}$ the half width of the selected absorption in wavenumber units of cm^{-1}. Fluorescence lifetimes are estimated as $\tau_f = \tau_o$. Q_f and the rates of fluorescence as $k_f = 1/\tau_o$. As seen the radiative lifetimes of I–III are in 5.6–6.7 ns limits and the fluorescence lifetimes are 0.1 ns for I and III, and 0.9 ns for 4-methyl-6-hydroxy-(5,6)-benzocoumarin, II. The singlet lifetime of 7-dimethylamino-4-methylcoumarin is reported to be in a similar range, $\tau_s = 3$ ns [26]. The fluorescence rates of the studied compounds of I, II and III are calculated to be 1.5×10^7, 1.8×10^7 and 1.7×10^7 s^{-1}, respectively.

Hamanoue et al. reports a triplet lifetime of 0.3 μs of 4-chromanone in benzene [27], may be taken as evidence for the formation of singlet oxygen from triplet state. In accordance with, the formation of singlet oxygen for benzocoumarins I and II were detected. At singlet oxygen quantum yield (ϕ_Δ) determinations, the decays were curve fitted and the intensities at $t = 0$ were taken. The absorptivity values of I, II and reference (phenazine) is computed via absorptivity $= 1 - 10^{-A}_{355}$ and a graph, intensity versus absorptivity values for four points with three parallel measurements was drown (Fig. 5). From the slopes of the curves the ϕ_Δ values for I and II were calculated as 0.15 and 0.40, respectively (Table 2).

3.2. Fluorescence quenching and cyclic voltametric studies

Fluorescence quenching studies were carried out by addition of acetonitrile solutions of benzocoumarins, I and II, and benzochromone, III, into acetonitrile solution of anthracene, and observing the quenching of anthracene fluorescence at $\lambda_{exc} = 339$ nm, $\tau^{ANT}_T - 339$ ms. As seen in Fig. 1, anthracene fluorescence emission declined by the addition of 4-methyl-8-hydroxy-benzo(6,7)coumarin, I, and the fluorescence of emission of I increased to 450 nm. All three compounds have shown quenching rates below the diffusion limits, 10^7–10^9 M^{-1} s^{-1}, calculated from Stern–Volmer plots. Benzo(5,6)coumarin, II, which gives the most intense fluorescence among the three compounds, also presents the highest quenching rate, $k_q = 1.2 \times 10^9$ M^{-1} s^{-1}. In agreement with, chromone fluorescence emission is reported to be quenched at rates of 10^8–10^9 M^{-1} s^{-1} by cupric and nitrite ions in water and it was proven that a triplet state quenching is in progress [28]. Coumarines are known to be also triplet sensitizers [29]. These results may indicate that benzocoumarins and benzochromone I–III behave as electron acceptor moieties against a condensed aromatic ring, anthracene. The planarity of the benzocoumarin and the benzochromone rings and the presence of electron withdrawing groups of hydroxyl and carbonyl may have caused the donor–acceptor interaction. One may expect

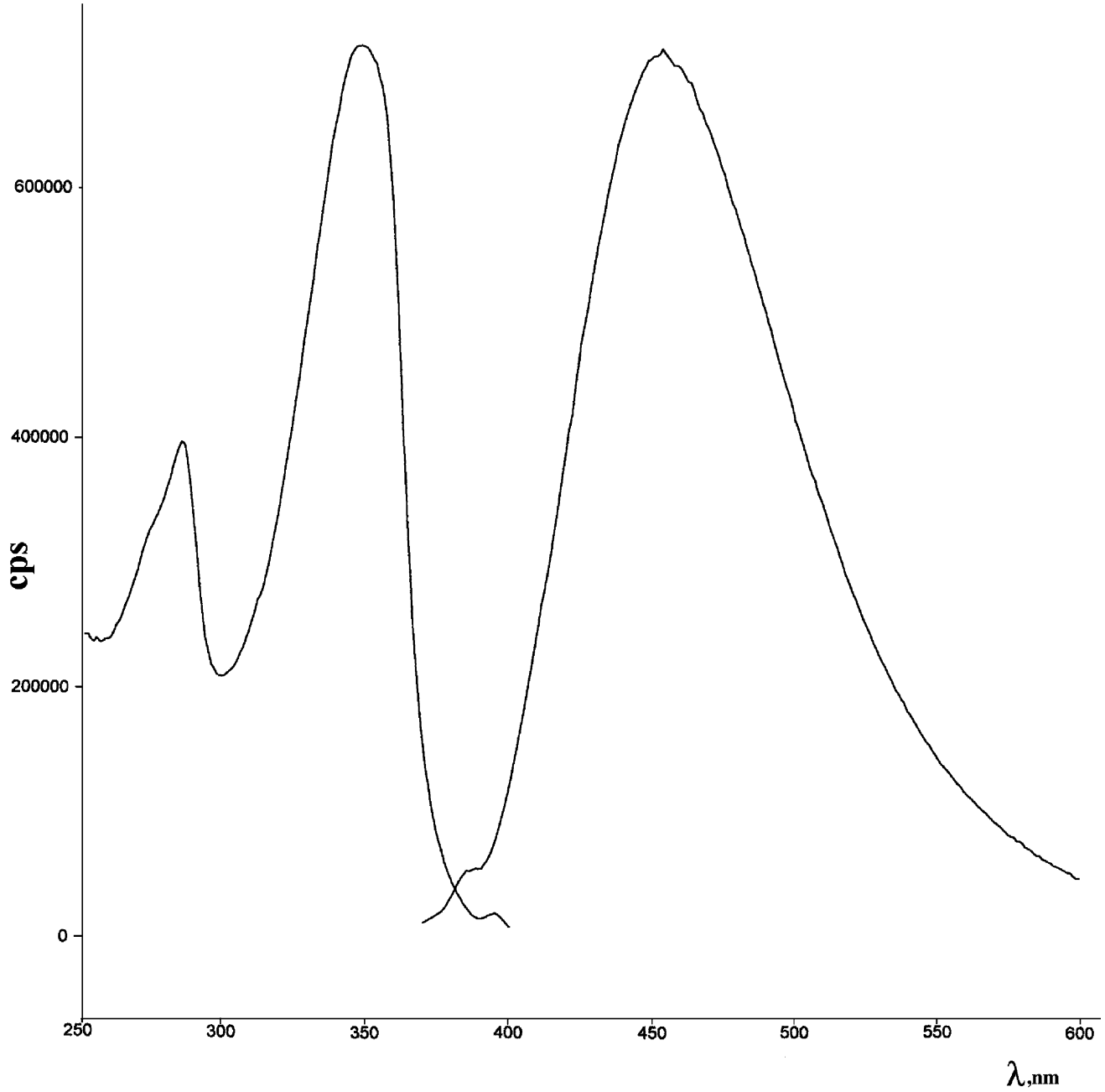


Fig. 4. Fluorescence emission band $\lambda_{ext} = 343$ nm, and excitation band, $\lambda_{em} = 450$ nm, of benzocoumarin I in acetonitrile solution.

the formation of contact ion pairs resulting from electron transfer between a donor molecule and benzocoumarin or benzochromone under photolysis. Intersystem crossings to triplet energy level in coumarins is known in the literature, 7-dimethyl-amino-4-methylcoumarine is measured to have a triplet lifetime of $\tau_T = 3300\ \mu s$ [30,31]. It may be expected that benzocoumarins of I, II and benzochromone III could produce singlet oxygen on photolysis. The triplet energy of both coumarin and 7-dimethylamino-4-methylcoumarin is reported to be 62.2 kcal/mol [23,25], and of chromone 75.1 kcal/mol [27]. If one assumes similar triplet energies for the three studied compounds, the singlet–triplet energy gap in benzocoumarins of I and II would be approximately 20 kcal/mol and the benzochromone III derivative would be about 10 kcal/mol. These high singlet–triplet energy gaps may suggest that benzocoumarins and benzochromones could be taken as singlet sensitizers as well as the triplet sensitizers.

Comparing the values in Table 3, it is seen that $E(A/A^-)$ of I–III becomes less negative as the k_q values gradually increase. Quenching data can be analyzed by using

$$\Delta G_{ET}(\text{kcal/mol}) = 23.06[E(D^+/D) - E(A/A^-)] - E_D^*$$

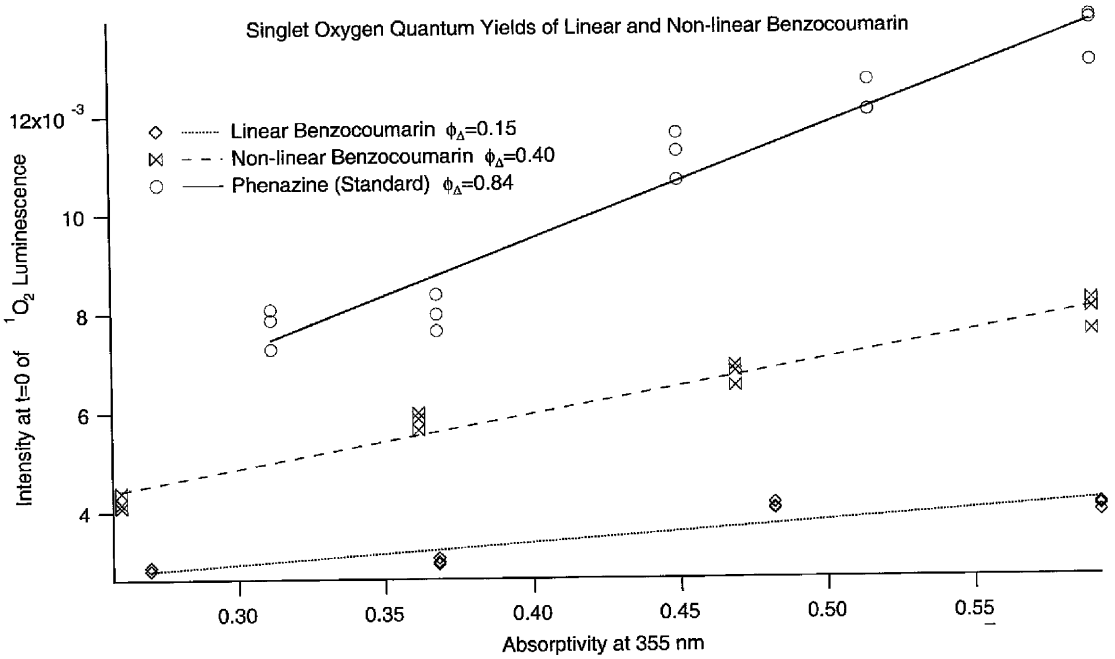


Fig. 5. Singlet oxygen quantum yields of I and II, relative to phenazine.

equation [32], with which the free energy change for an encounter pair undergoing electron transfer is computed by using redox potentials, and where E_D^* is the excitation energy of the excited state participating in quenching. Computed free energies are also provided in Table 3. The ΔG_{ET} values are all ≤ -5 kcal/mol (the "rule of thumb", [33]) and may account for a favorable electron transfer between the anthracene and I–III. Benzocoumarin, II, which has the highest fluorescent quantum yield and the highest fluorescence quenching rate among the three studied compounds, and has the lowest free energy of electron transfer, $\Delta G_{ET} = -9.4$ kcal/mol. It may be concluded that benzocoumarin, II, has the most favorable structure for photo electron transfer. Jones II and co-workers reports that a condensed rings substituted coumarine derivative gives higher quenching rates in cyclodextrins because of an increase on excited state life times [34]. Similar argument may be correlated to benzocoumarin, II.

3.3. Photooxidation studies

α-Terpinene is known to produce endoperoxide (ascaridole) adduct on photooxidation with triplet sensitizers. It is also proven that in presence of perylene and naphthalene diimides α-terpinene is converted to *p*-cymene under visible irradiation [19,37]. A singlet state electron transfer in an exciplex that forms hydroperoxide radicals reaching to *p*-cymene in radical chain reactions was proposed for the mechanism. Chen et al. performed the photooxidation of α-terpinene by a perylene diimide derivative and their results indicated a novel photooxidation that proceeds via an initial electron transfer quenching of the singlet dye by diene, followed by a reaction of the exciplex with oxygen [19]. Product analysis on dye sensitized photooxidation of α-terpinene would give evidences to presence of singlet oxygen and/or photo electron transfer mechanisms.

Table 3
Fluorescence quenching rate constants of anthracene donor molecules by the addition of I, II and III, redox potentials and E_{00} energies of the acceptors and donors in acetonitrile

Acceptor	Compound			Donor (anthracene)
	I	II	III	
k_q ($M^{-1}\,s^{-1}$)	1×10^7	1.2×10^9	6.1×10^7	
E_{00} (kcal/mol)	83.62	82.65	85.11	84.11
E (V vs. Ag/AgCI)	−1.041	−0.98	−0.998	−2.259[a]
ΔG_{ET} (kcal/mol)	−8.0	−9.4	−9.0	

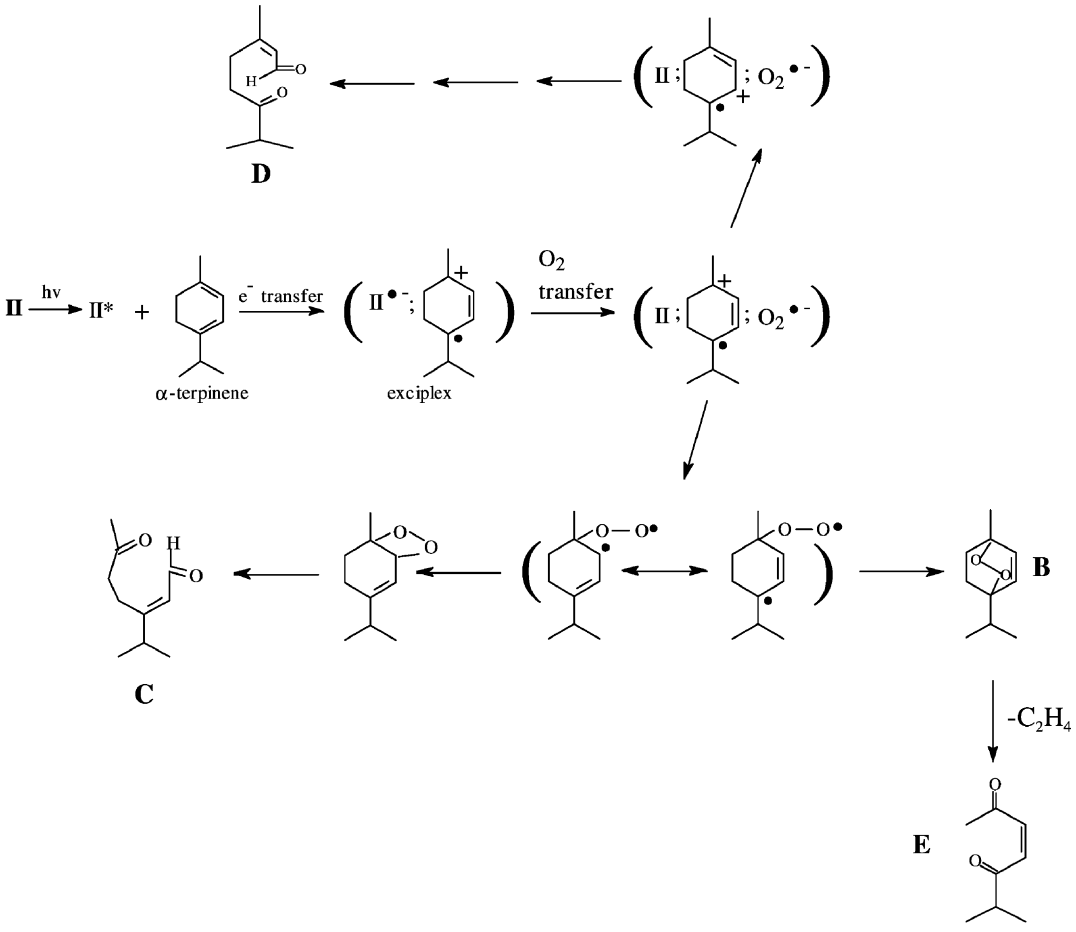
[a] Value obtained from Handbook of Analytical chemistry [35] vs. hydrogen electrode was computed though $E_{cell} = E_{ind} - E_{ref}$; E_{ref} for Ag/AgCl is 0.199V [36].

Table 4
Yields in % ratios of A–E from the photooxidation of α-terpinene in acetonitrile solution in the presence of II

Irradiation source	Photooxidation period (h)	A (%)	B (%)	C (%)	D (%)	E (%)
Direct sunlight	33	22.4	39.7	18.1	3.0	6.1
Concentrated sunlight	4	39.9	26.9	7.2	2.0	3.4
Concentrated sunlight	0.25	48.6	8.3	5.6	–	1.4

In our case, 4-methyl-6-hydroxy-benzo(5,6)coumarine, II that has the most intense fluorescence emission, $\phi_f = 0.16$ is selected as sensitiser and the photoxoidation reactions are performed under direct and concentrated sunlight of 130–150 suns. GC–MS results are given in Table 4. Consumption of α-terpinene was followed by TLC during the progress of solar irradiation. α-Terpinene was converted completely to products after 4 h of irradiation under concentrated sun light of 130–150 suns. Scheme 1 outlines the photo electron transfer mechanism of formation of ascaridole, B, 3-isopropyl-2-heptenal-6-one, C, 3,7-dimethyl-2-opctenal-6-one, D and 6-methyl-2,5-dion-3-heptene, E that are the photooxidation products of α-terpinene. The mechanism of formation of *p*-cymene, A, on photooxidation of α-terpineneis being shown in literature earlier [30,31]. Photolysis of α-terpinene in nitrogen bubbled solution for 4 h with coumarine II, under concentrated sun light of 130–150 suns, yielded no products. Photoelectron transfer appear as not taking place in absence of oxygen. This result is in support of the mechanism in Scheme 1.

Direct sunlight photooxidation of α-terpinene in presence of II yielded a total of 45.8% singlet oxygen products (B and



Scheme 1.

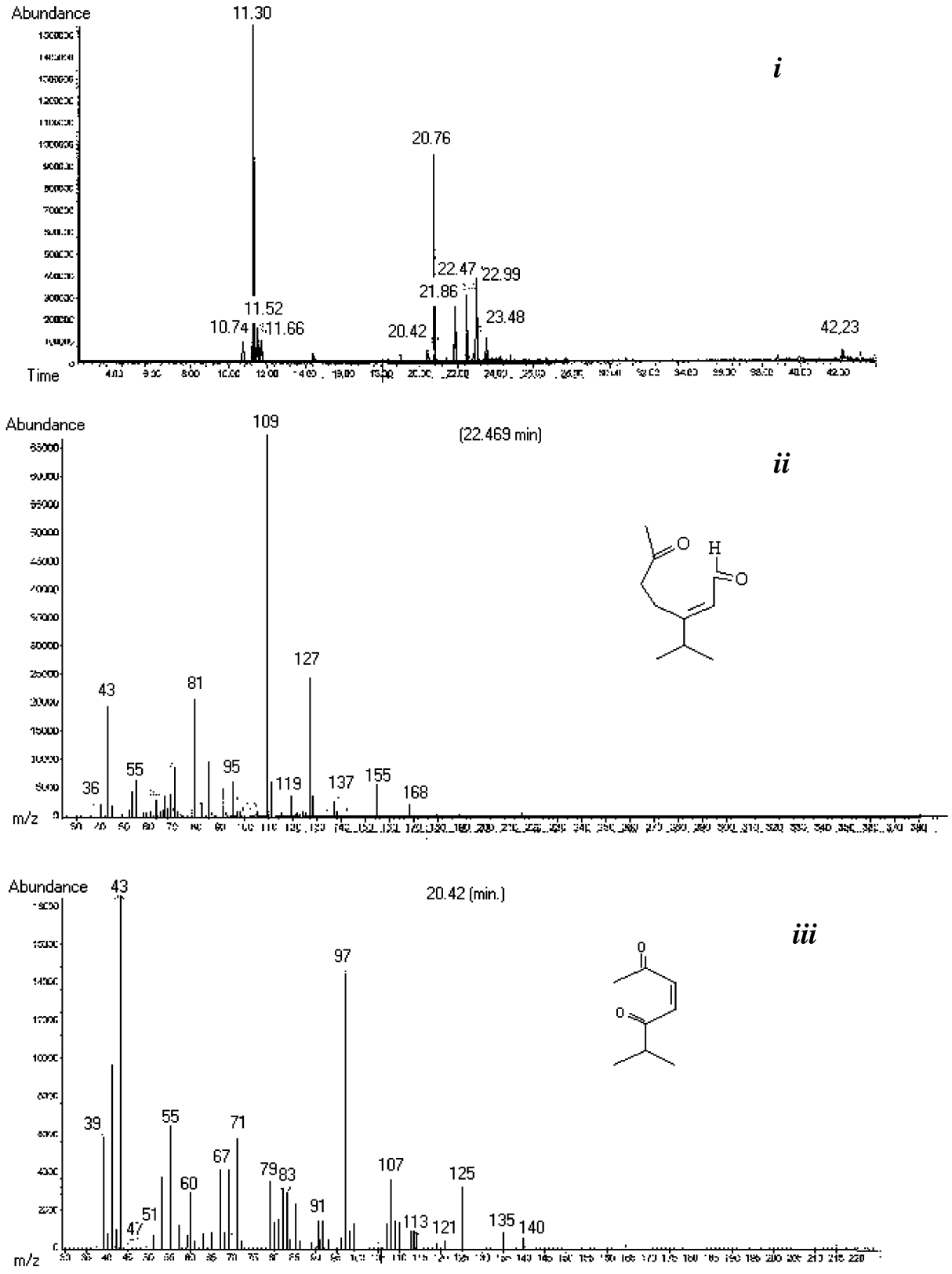


Fig. 6. Retention time vs. abundance for the concentrated sunlight experiment carried out for 15 min (i), mass spectrum of 3-isopropyl-2-heptenal-6-on (C) (ii) and 6-methyl-2,5-dion-3-hepten (E) (iii).

E) and total of 43.5% of superoxide anion radical products (A, C, D) in total. *p*-Cymene, A, superoxide anion radical, $O_2^{\bullet -}$, product appear to be the dominant one, at 22.4% ratio, the other ring opened products of C and D are at 18.1 and 3.0% ratios, respectively (Table 4). Although the product types are found to be the same under direct and concentrated sun light irradiations, but the product ratios are found to be different (Table 4, Figs. 1 and 6). Ascaridol, B and E are produced at 26.9 and 3.4% ratios, respectively (total of 31.3%), and *p*-cymene A, ring opened products of C and D are produced at 39.9, 7.2 and 2.0% ratios, respectively (total of 49.1%). Irradiation of α-terpinene under concentrated sun light of 130–150 suns for 0.25 h (15 min) yielded products of A, B,C, E and unconsumed α-terpinene (retention time: 20.76 min s) in 17.1% ratio (Fig. 1). α-Terpinene was completely consumed after 4 h of concentrated sun light irradiation (Fig. 6). Concentrated sun light irradiation for 4 h increased the ratios of ring opened products of C–E, but as well as the ratio of ascaridol, B which is assumed to be the dominant product of singlet oxygen. On the other hand, the relative ratio of *p*-cymene, A, primary product of super oxide anion radical, $O_2^{\bullet -}$, decreased after 4 h of irradiation. This result may indicate that ascaridol, B, and the secondary product of E, could have been produced by the reaction of super oxide anion radical, $O_2^{\bullet -}$, through a photo electron transfer mechanism (Scheme 1), as well as from the reaction of singlet oxygen. It is well-known in literature that the lifetime of $^1O_2$ can vary from 3 to 1000 μs depending on the nature of the medium and is very reactive oxidation agent [38]. One may expect a higher ratio than 8.3% for the formation of ascaridol, B, after 15 min of concentrated sun light irradiation, if benzo(5,6)coumarine was an efficient triplet sensitizer and produced only singlet oxygen (Table 4).

All of these results may prove that photooxidation of benzocoumarins proceed through both triplet and singlet state electron transfer to oxygen in an exciplex. Benzocoumarins are also stable photosensitizers under intense solar irradiations of 150 suns for hours. The existence of benzocoumarins and benzochromones in natural organisms and their biological activities, may be related to their effective photooxidation capacities.

4. Conclusion

UV absorption spectra are found to be consistent with each other for I–III. Fluorescence emission is found to increase from linear benzocoumarin, I, to non-linear benzocoumarin, II, but replacement of carbonyl and methyl groups in the non-linear benzochromone, III, has lowered the fluorescence emission, with respect to non-linear benzocoumarin, II. These results prove that basic structural variations can play a dominant role on the luminescence properties of benzocoumarins and benzochromones.

Irradiation time and intensity of irradiation has an important effect on the product pattern. Benzocoumarin derivative used in photooxidation reaction is capable of producing both singlet oxygen and superoxide anion radical; therefore in good agreement with literature data benzocoumarins can be named as both triplet and singlet sensitizers.

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References

[1] B.M. Krasovitskii, B.M. Bolotin, Organic Luminescent Materials, VCH GmbH, Weinheim, Germany, 1988.
[2] T. Hiroshi, O. Yosho, I. Juzo, I. Masato, T. Atsushi, Jpn. Kokai Tokkyo Koho, 1990. CODEN: JKXXAF JP 02126241 A2 19900515 Heisei.
[3] H.E. Patel, K.R. Desai, J. Inst. Chem. 68 (3) (1996) 78.
[4] O.D. Korotchenko, S.M. Alekseev, R.P. Evstigneeva, G.V. Karpova, S.V. Isai, Chem. Nat. Compd. 35 (6) (2000) 612.
[5] E.-K. Seo, M.C. Wani, M.E. Wall, H. Navarro, R. Mukherjee, N.R. Farnsworth, A.D. Kinghorn, Phytochemistry 55 (1) (2000) 35.
[6] M. Iinuma, J. Yokoyam, M. Ohyama, T. Tanaka, N. Ruangrungsi, Phytochemistry 35 (3) (1994) 785.
[7] M.M. Marchenko, G.P. Kopylchuk, O.V. Grigoreva, Dopov. Akad. Nauk. Ukr. 3 (2000) 192.
[8] M. Mazzei, E. Sottofattori, M. Ibrahim, A. Balbi, Nucleosides Nucleotides 17 (9–11) (1998) 1885.
[9] Z.-Q. Liu, W. Yu, Z.-L. Liu, Chem. Phys. Lipids 103 (1999) 125.
[10] E.B. Kim, G.J. Zylstra, T.M. Heinze, J. Deck, C.E. Cerniglia, Fems Microbiol. Lett. 153 (2) (1997) 479.
[11] M. Grifoll, S.A. Selifonov, P.J. Chapman, Appl. Environ. Microbiol. 60 (7) (1994) 2438.
[12] W. Adam, A.G. Griesbeck, in: W.M. Horspool, P.-S. Song, (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, CRC Press, Boca Raton, FL, 1994, pp. 311–324.
[13] J. Rigaudy, in: W.M. Horspool, P.-S. Song, (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, CRC Press, Boca Raton, FL, 1994, pp. 325–334.
[14] M.I. Gutiérrez, A.T. Soltermann, F. Amat-Guerri, N.A. Garc, J. Photochem. Photobiol: A Chem. 136 (2000) 67.
[15] K. Song, L.Z. Wu, C.H. Yang, C.H. Tung, Tetrahedron Lett. 41 (2000) 1951.
[16] N. Soggiu, H. Cardy, J.L.H. Jiwan, I. Leray, J.P. Soumillion, S. Lacoube, J. Photochem. Photobiol: A Chem. 124 (1999) 1.
[17] H.R. Li, L.Z. Wi, C.H. Tung, Tetrahedron Lett. 56 (2000) 7437.
[18] M. Bera, A. Rivaton, C. Gandon, J.L. Gardette, Eur. Polym. J. 36 (2000) 1753.
[19] L. Chen, L.A. Lucia, E.R. Gaillard, H. Icil, S. Icli, D.G. Whitten, J. Phys. Chem. A102 (1998) 9095.
[20] H. Kolancýlar, Ph.D. Thesis, Synthesis and studies in benzocoumarin and benzochromone systems, Trakya University, Edirne, Turkey, 1999.
[21] T.V. Sakhno, I.V. Korotkova, O.A. Khakhel, Teor. Eksp. Khim. 32 (4) (1996) 247.
[22] R.W. Rechmond, S.E. Braslavsky, NATO ASI Ser. Ser H 15 (1988) 93–95.

[23] T.A. Moore, M.L. Harter, P.-S. Song, J. Mol. Spectrosc. 40 (1971) 144.
[24] A. Gaplovsky, J. Donovalova, M. Lacova, R. Mracnova, J. Chovancova, J. Photochem. Photobiol. B: Biol., http://www.photobiology.com/photobiology99, 16 July–7 September 1999, papers and posters.
[25] G. Jones II, W.R. Jackson, C. Choi, W.R. Bergmark, J. Phys. Chem. 89 (1985) 294.
[26] G. Jones II, W.R. Jackson, A.M. Halpern, Chem. Phys. Lett. 72 (1980) 391.
[27] K. Hamanoue, T. Nakayama, T. Miyake, H. Teranishi, Chem. Lett. (1981) 39.
[28] M. Christoff, L.T. Okano, C. Bohne, J. Photochem. Photobiol. A: Chem. 134 (2000) 169.
[29] V.S. Sharov, E.S. Driomina, K. Briviba, H. Sies, J. Photochem. Photobiol. A: Chem. 68 (6) (1998) 797.
[30] J.B. Gallivan, J.S. Brinen, Chem. Phys. Lett. 10 (1971) 455.
[31] E.J. Land, T.G. Truscott, Photochem. Photobiol. 29 (1979) 861.
[32] G.J. Kavarnos, N.J. Turro, Chem. Rev. 86 (1986) 401.
[33] G. Jones II, S.F. Griffin, C. Choi, W.R. Bergmark, J. Org. Chem. 49 (1984) 2705.
[34] W.R. Bergmark, A. Davis, C. York, A. Macintosh, G. Jones II, J. Phys. Chem. 94 (1990) 5020.
[35] L. Meites, Handbook of Analytical Chemistry, Mc-Graw-Hill, New York, 1963.
[36] D.A. Skoog, D.M. West, F.J. Holler, Fundamentals of Analytical Chemistry, 7th ed., Saunders, London, 1996.
[37] S. Alp, S. Erten, C. Karapire, B. Koz, A.O. Doroshenko, S. Icli, J. Photochem. Photobiol. A: Chem. 135 (23) (2000) 103.
[38] A. Gilbert, J. Baggott, Essentials of Molecular Photochemistry, Blackwell Scientific Publications, Oxford, 1991, pp. 502–503.