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Selective laser photolysis of organic molecules in complex matrices

C. Moulin[a,*], A. Petit[a], J.C. Baccou[b]

[a]*CEA-DCC/DPE/SPEA/Section de Photoionisation et de Spectroscopie, CE Saclay, 91191 Gif sur Yvette Cedex, France*
[b]*Laboratoire de Physiologie Végétale, Université de Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex, France*

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Abstract

Laser photolysis was used to eliminate selectively non- desirable (toxic, carcinogenic, photosensitive) molecules in complex solutions for applications in various fields, such as the farm-produce industry, cosmetics, perfumes or biology. The principle of this experiment is based on the tuning of the laser wavelength to an absorption band of the non-desirable molecules which are excited and then dissociated. Destruction of the molecules is monitored by spectral changes, and photoproducts can be characterized by gas chromatography and mass spectrometry. The advantages of this technique are its rapidity, in situ reaction and quantitative elimination. Examples including the destruction of thujone in extract of Salvia, bergapten in essential oil of Bergamot, safrole in essential oil of Sassafras and phycocyanin and phycoerythrin in *Porphyridium cruentum* are presented and discussed.

Keywords: Laser photolysis; Organic molecules; Complex matrices

1. Introduction

Photochemistry has been used in various fields of investigation (medicine, industrial synthesis, agriculture, polymers) for many decades. At the beginning, classical sources such as the sun and then lamps (visible, UV or IR) were used in various processes, such as psoriasis treatment, water purification, polymer formation and photonitrosation [1–3]. Lasers in the various fields of chemistry are receiving increasing interest since photochemical methods are more selective and less aggressive than thermal reactions [2–4]. Hence laser photochemistry has been used to understand complex phenomena, such as transient radical [5], fragmentation [6,7] and molecular [8] dynamics. Since the pulse duration of lasers has improved from nanoseconds to picoseconds and, more recently, to several femtoseconds, it is possible to observe phenomena such as bond breaking, electron transfer or solvent stabilization of excited states [9].

Laser sources can also be used as powerful tools to destroy molecules selectively and thus purify complex mixtures. This procedure has been applied mainly for gas purification, such as $AsCl_3$ [10] (removal of $C_2H_4Cl_2$ and CCl_4 with CO_2 laser) or SiH_4 [11] (removal of PH_3, AsH_3 and B_2H_6 with ArF laser), but few applications have been reported for solutions. Natural extracts or essences are largely used in the farm-produce industry, cosmetics, perfumery, biochemistry and chemistry. Purposes are various from unguents, flavouring agents and perfumes to biocompatible dyes. However, most of these complex extracts also contain toxic, carcinogenic or non-desirable molecules. The usual way to eliminate these molecules is distillation for simple cases or, for more selectivity, separation techniques such as chromatography or electrophoresis. However, these very efficient separation techniques are time consuming, generate effluents and can lead to loss of product. As an alternative to separation techniques, direct destruction of the molecules by a photon-based method can be used. The purpose of this work was to study the direct and practical use of laser photolysis in the fields quoted above. Hence, by using a laser directly tuned to the absorption band of the unwanted molecule, single-photon or multiphoton processes can take place and lead to a predissociative state before final dissociation of the molecule. This process leads to the selective elimination of these molecules and may be of interest for these industries provided that the degradation products are safe.

*Corresponding author.

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Pulsed laser sources have numerous advantages compared with classical optical sources, e.g. power density, linewidth, tunability and coherence. The large difference in power may allow single- or multiphoton processes to take place leading to chemical bond breaking. Therefore the use of laser sources should allow fast and direct photolysis of organic molecules in solution. The advantages of this procedure include its rapidity, in situ reaction, the absence of chemical reagents and solvent (in certain cases) and the possibility to perform quantitative elimination (i.e. ability to stop the destruction process at any time). The main drawback (apart from the cost of products at low added value) is the need for a specific absorption band for the molecules to be eliminated in the complex solution. However, in the case of closely related absorption bands (due to the non- desirable molecules and molecules of interest), this drawback can be overcome by using a laser wavelength shifted from the absorption maximum (i.e. in the tail of the absorption band of the non-desirable molecule). By this means a certain selectivity can be obtained even in the case of overlapping absorption bands.

Laser photolysis has been used for the destruction of thujone in Salvia extract, safrole in essential oil of Sassafras, bergapten in essential oil of Bergamot and phycoerythrin and phycocyanin in *Porphyridium cruentum*. The results obtained on the selectivity and efficiency of the process for these different applications are presented.

2. Materials and methods

2.1. Laser photolysis

The experimental apparatus consisted of a dye laser (Lambda Physik, FL 2002) pumped by an excimer laser (Lambda Physik, EMG 203 MSC) operating at 308 nm (XeCl) and delivering about 200 mJ in a 25 ns pulse with a repetition rate adjustable from 1 to 200 Hz. The laser beam was sent directly into a quartz cell or circulation quartz cell (depending on the concentration) which contained the solution, and the output power before and after the cell was measured by a wattmeter (Scientech); this allowed in- line control of the elimination. Depending on the experiments, the excimer laser wavelength was used directly (thujone, bergapten, safrole) or the dye laser wavelength was employed: sulpho-rhodamine 101 (Exciton) for phycocyanin, laser energy 16 mJ; coumarin 102 (Exciton) for phycoerythrin, laser energy 22 mJ.

2.2. Spectrophotometry

The absorption spectra were obtained (Cary 17 spectrophotometer) for pure products and essential oils before and after laser photolysis, as well as several days after photolysis to observe whether or not the phenomena were reversible.

2.3. Gas chromatography (GC)

The solutions were analysed by GC on a DB1 column (length, 30 m; diameter, 0.25 mm) with hydrogen as gas vector. A temperature programme of 50 °C for 2 min followed by an increase of 4 °C min^{-1} until 280 °C was applied. The mixture was injected into the column at a temperature of 240 °C and the chromatogram was obtained with a flame ionization detector at 250 °C.

2.4. Mass spectroscopy

Products were characterized in certain cases by a quadrupole mass spectrometer (Hewlett Packard).

2.5. Reagents

The different molecules to be eliminated (thujone, bergapten, safrole (Sigma)) and the different essential oils (Salvia, Bergamot, Sassafras) were used as received, and laser photolysis was performed after appropriate dilution in ethanol (Merck): tenfold dilution for Salvia and Bergamot oils; hundredfold dilution for Sassafras oil. Phycobilisomes were used as received and laser photolysis was performed after a fivefold dilution in hydrogenphosphate buffer (Merck).

2.6. Procedure

For laser photolysis, classical quartz cells (Hellma) were used and, in certain cases (for high absorption), a quartz flow cell with thermoregulation was employed to avoid thermal heating. First, single unwanted molecules were photolysed at various dilution factors in the solvent in order to determine the efficiency of the destruction and then essential oils were photolysed in the same way to determine the selectivity of the process. The average volume for laser photolysis was 2 ml. In all the experiments, no attempt was made to exclude air.

3. Results and discussion

Initially, both the absorption spectrum of the molecule to be destroyed and the absorption spectrum of the complex solution were recorded. Secondly, when the optimum absorption band (in terms of the wavelength separation from the other products and the maximum extinction coefficient) had been selected, the laser was tuned to this particular band and laser photolysis was started. One interesting feature in all cases which

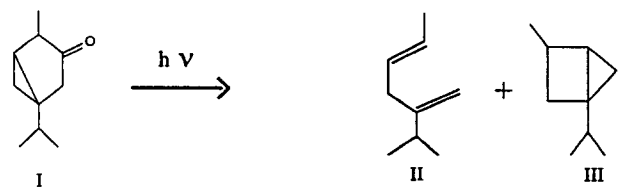
facilitates destruction (especially in terms of selectivity) is that most of the molecules to be eliminated have higher absorption wavelengths (due to conjugation) than most of the other constituents. Destruction of the unwanted molecules was observed by monitoring the laser energy after the cell, which should be the same as the energy before the cell when all the unwanted molecules have been eliminated. This particular absorption monitoring is only possible when the molecules to be eliminated are present at a large concentration or have a large extinction coefficient. However, this procedure is only qualitative and, in all cases, the efficiency of the destruction and the products formed were analysed and eventually characterized by GC and mass spectroscopy.

3.1. Destruction of thujone in Salvia extract

Salvia (*Salvia officinalis*) extract possesses very interesting anti-oxidant properties for the farm-produce industry, but its use is limited due to the presence of thujone. Thujone ($C_{10}H_{16}O$) is a monoterpene ketone present in numerous essential extracts (thuja, red cedar, Salvia); it is a very toxic compound responsible for the noxiousness of the liqueur absinthe. In Salvia extract, thujone (α, β) is one of the major constituents with camphor: 46% ($\lambda_{max}=290$ nm, $n\rightarrow\pi^*$ band) and 18% ($\lambda_{max}=290$ nm, $n\rightarrow\pi^*$ band) respectively. The other main constituents are cineol (12%), pinene (α, β) (4.5%) ($\lambda_{max}=210$ nm), α-humulene (4.3%), β-caryophyllene (3.1%) ($\lambda_{max}=280$ nm), camphene (2.6%) ($\lambda_{max}=206$ nm) and borneol (2.4%).

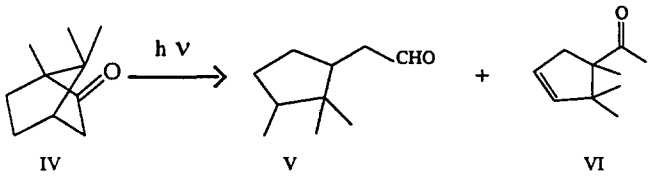
Since the absorption coefficient of thujone at 308 nm (XeCl excimer wavelength) is still very high, direct laser photolysis at 308 nm was performed. The photoproducts formed were analysed by GC and the results obtained are presented in Table 1. Laser photolysis of thujone (**I**) gives two main products (84%) at short retention times (3.9 and 4.05 min) which have a molecular weight of 124 (determined by mass spectrometry) and are due to the elimination of carbon monoxide in thujone to yield **II** and **III**.

This process is well known for cyclic ketones and thujone on UV irradiation [12–14] and the following reaction has been reported where the driving force is the relief of ring strain. The mechanism of formation probably involves Norrish type I cleavage, loss of CO from the resulting radical and recombination of the radical fragments [15].



I II III

Fig. 1 presents the absorption spectra of Salvia extract before and after photolysis at 308 nm. It can be seen that the peak at 290 nm has completely disappeared, as confirmed by the results obtained by GC (Table 1), where the thujone concentration is decreased by two orders of magnitude with the same ratio of products formed as for pure thujone. However, the most important feature is that most of the other molecules present, such as pinene, camphene, cineol, borneol, caryophyllene and humulene, have not been destroyed. The only other product that also disappears is camphor, which is expected since it is also a ketone with a very similar structure to thujone and hence a very similar absorption spectrum. The photolysis of camphor (**IV**) in alcoholic solution with a UV lamp has been performed [14,16] and the following reaction has been reported leading to products **V** and **VI**



IV V VI

During laser photolysis, these products (Table 1) were identified with retention times of 15.5 and 16.2 min, but with a low percentage (2.1% and 2.6%) compared with the initial percentage of camphor (18.2%); as will be seen from the other examples, the products formed under high laser intensity are, in most cases, of lower molecular weight than the initial products. However, in the case of Salvia extract, a new product (8.7%) appears with a high retention time (21.1 min), implying a higher molecular weight than thujone and camphor, probably due to rearrangement with the solvent (EtOH). The absorption spectra taken several days after laser photolysis present no differences showing that this process is irreversible.

3.2. Destruction of bergapten in Bergamot oil

Bergamot oil is produced from mechanical treatment of the skin of *Citrus aurantium bergamia* [17]. This green extract with a sweet odour is used in perfumery, in particular for eau- de-Cologne. However, its use is restricted due to the presence of bergapten. Hence bergapten ($C_{12}H_8O_4$, 5-methoxypsoralen, **VII**), a furocoumarin, is responsible for phototoxic reactions when skin covered with Bergamot is exposed to UV light. The proposed mechanism proceeds through the cycloaddition (at the 3,4-double bond) of bergapten with the pyrimidine base of DNA [18,19], and it has been reported that its concentration should be reduced to lower than 0.001% [20]

Table 1
GC analysis of thujone and Salvia extract before and after laser photolysis at 308 nm (only percentages greater than 0.5% are presented). Tenfold dilution in ethanol; laser photolysis time, 10 min; laser repetition rate, 20 Hz; laser intensity, 200 mJ

Retention time (min)	Thujone (%)	Thujone after photolysis (%)	Salvia extract (%)	Salvia extract after photolysis (%)
2.1		2.8	–	6.2
3.9		71.6	0.5	35.8
4.05		12.1	–	6.2
4.64		3.3	–	–
5.84 (α-pinene)		–	2.7	2.8
6.13 (camphene)		–	2.6	2.8
6.95 (β-pinene)		–	1.8	1.7
8.43 (cineol)		–	12.1	13.2
10.82 (β-thujone)	75.2	–	42	0.5
11.22 (α-thujone)	15.2	–	3.8	–
11.84 (camphor)		–	18.2	–
12.83 (borneol)		–	2.4	3.3
15.5/16.2/21.1		–	–	2.1/2.6/8.7
21.9 (β-caryophyllene)		–	3	2
23.1 (α-humulene)		–	4.3	3.1
27.12		–	2.6	2.5

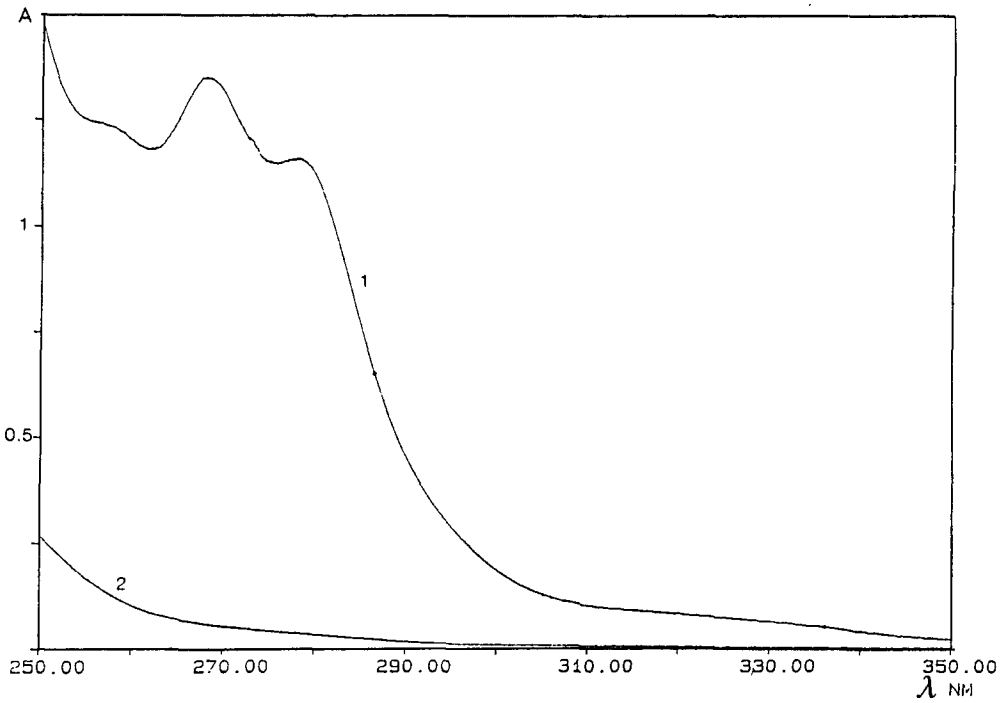
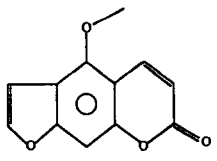


Fig. 1. Absorption spectra of Salvia extract before (1) and after (2) laser photolysis at 308 nm. Laser photolysis time, 10 min; laser repetition rate, 20 Hz; fiftyfold dilution in ethanol.



VII

This molecule has been extensively studied by IR, UV and nuclear magnetic resonance (NMR) spectroscopy and chromatography [21–23]. The interesting feature of bergapten is that one of its absorption maxima (311 nm, $\epsilon = 63$ l mol^{-1} cm^{-1}, $\pi \rightarrow \pi^*$ band) is close to the excimer laser wavelength. The other maxima are at 233, 243, 259 and 268 nm. Fig. 2 presents the absorption spectra of Bergamot oil before and at various times during laser photolysis at 308 nm. The peak at 311 nm, characteristic of bergapten, progressively disappears and there is a decrease in the other maxima in the region 240–270 nm. Bergamot oils after photolysis

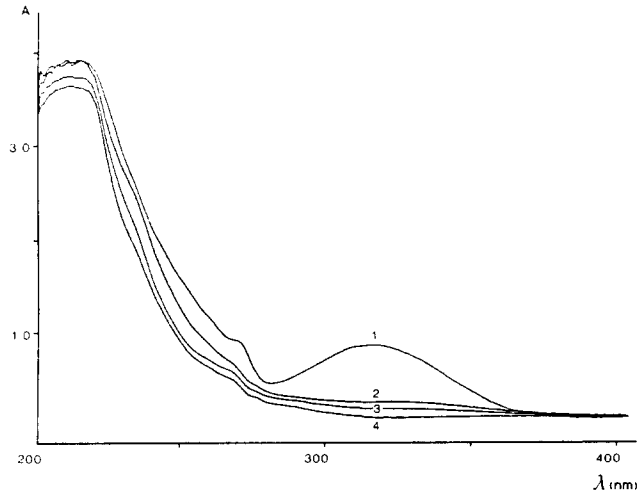
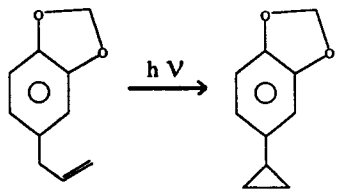


Fig. 2. Absorption spectra of oil of Bergamot before (1) and after (2, 3, 4) laser photolysis at 308 nm. Laser photolysis time, 3 min (2), 5 min (3), 10 min (4); laser repetition rate, 20 Hz; tenfold dilution in ethanol.

were analysed by GC. After 1 h of photolysis at 10 Hz, 35% of bergapten is destroyed; after 2 h, 60% is destroyed. The other products present are not affected. Longer photolysis times or higher laser repetition rates lead to the complete destruction of bergapten. Thus progressive destruction can be performed and a certain percentage of the molecule can be left in solution. This is of particular interest in the farm-produce industry where flavouring agents, such as essential oils, can be used with the percentage of "toxic molecules" perfectly regulated. Absorption spectra performed several days after laser photolysis again present no differences showing the irreversibility of the process.

3.3. Destruction of safrole in oil of Sassafras

Oil of Sassafras is obtained from water distillation of roots of *Ocotea pretioza mez* or can be extracted from *Laurus sassafras* [24,25]. Applications of this extract are in medicine (as revulsant or unguent) and cosmetics (for perfumes or soaps) and, in the past, in soft drinks and ice-creams. However, its use is restricted due to the presence of safrole, a carcinogen [26], the content of which in oil of Sassafras varies from a few per cent to 70%. Safrole ($C_{10}H_{10}O_2$) (**VIII**), on UV photolysis, forms 1- cyclopropyl-3,4-(methylenedioxy)benzene (**IX**) [27]



VIII IX

The absorption spectrum of safrole in ethanol is characterized by two bands at 236 nm ($\epsilon = 4180$ l mol^{-1} cm^{-1}, K band, n→π and π→p) and 285 nm ($\epsilon = 3770$ l mol^{-1} cm^{-1}, B band, benzenoid) [28–30]. Oil of Sassafras has a very similar absorption spectrum to safrole since the latter represents 65% of the product. The other main constituents are hydrocarbons (mono- and sesquiterpenes), phenols and ketones. Since, it is not possible to tune the laser wavelength to 285 nm, direct photolysis at 308 nm was performed.

Fig. 3 shows the absorption spectra of oil of Sassafras before and after laser photolysis at 308 nm; it can be seen that the peaks at 285 and 236 nm disappear. The peak which is still present at 280 nm at the end of laser photolysis is due to the other constituents. Chromatograms of oil of Sassafras before and after laser photolysis show the complete disappearance of the safrole peak (retention time, 16 min) and the appearance of three main peaks at retention times of 1.9, 2.2 and 2.3 min. These peaks were not characterized by mass spectroscopy but, due to their very short retention times, can be assumed to be short fragments of the safrole molecule.

Due to the large difference in energy, this result is very different from that obtained with a UV lamp [27]. In most of these applications, as expected, the use of a high intensity laser for photolysis leads to photoproducts of lower molecular weight. Such a phenomenon is well known in photopolymerization where high laser peak power decreases the molecular weight distribution [31].

3.4. Destruction of phycocyanin and phycoerythrin in Porphyridium cruentum

Porphyridium cruentum is a unicellular red alga of the group Rhodophyceae. It is composed of granules: phycobilisomes which correspond to the aggregation of phycobiliproteins [32–34]. The former consist of 84% of phycoerythrin, 11% of phycocyanin and 5% of allophycocyanin. Phycobilisomes can be used as fluorescent tracers in immunology (tag for an antigenic tracer in a cellular preparation by the association of a specific antibody). This tracer has several advantages compared with classical fluorescent tracers such as fluorescein: high excitation and fluorescence quantum yield, constant fluorescence over a large pH range, red–orange fluorescence (minimum interference with other organic compounds), high water solubility and biocompatibility. The purification and separation of phycobiliproteins requires several chromatographic steps and leads to loss of product. Thus laser photolysis was used to eliminate selectively phycocyanin and phycoerythrin in *Porphyridium cruentum*.

Fig. 4 presents the absorption spectra of phycobilisomes before and after laser photolysis (at various times) at 620 nm. The spectrum above 500 nm consists of two main bands at 549 and 619 nm which are

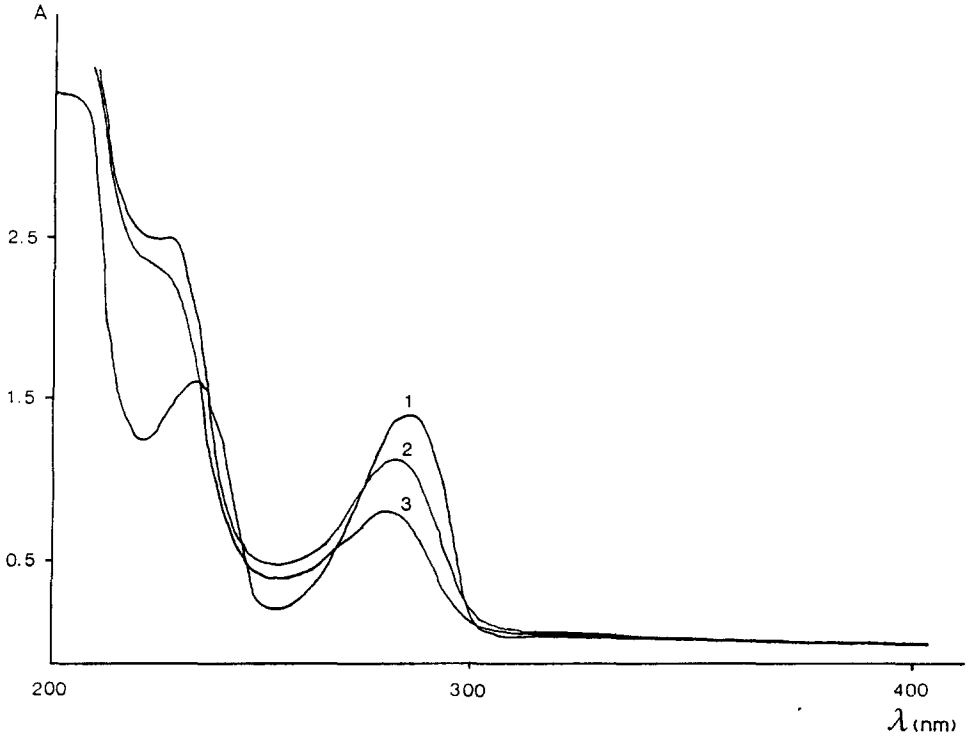


Fig. 3. Absorption spectra of oil of Sassafras before (1) and after (2, 3) laser photolysis at 308 nm. Laser photolysis time, 15 min (2), 30 min (3); laser repetition rate, 20 Hz; two hundredfold dilution in ethanol.

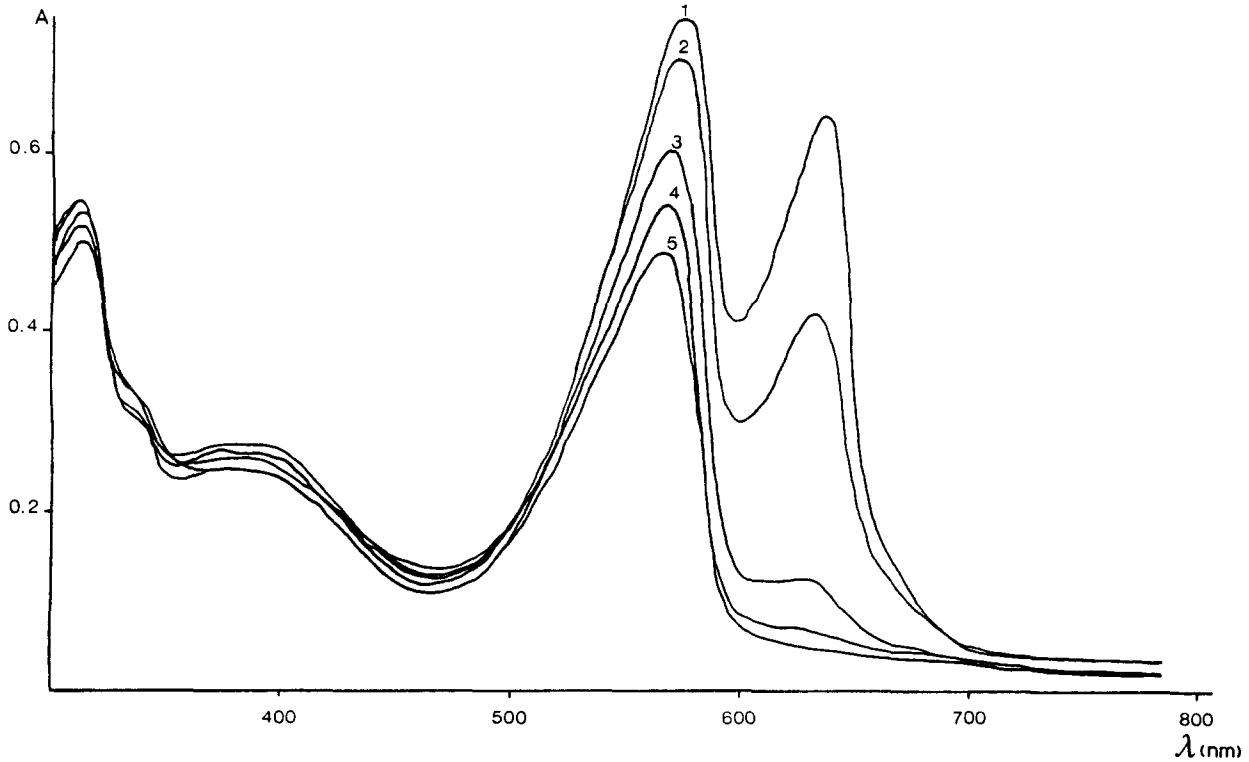


Fig. 4. Absorption spectra of phycobilisomes before (1) and after (2–5) laser photolysis at 620 nm for phycocyanin destruction. Laser photolysis time, 2 min (2), 5 min (3), 10 min (4), 15 min (5); laser repetition rate, 100 Hz; laser intensity, 22 mJ; fivefold dilution in hydrogenphosphate buffer.

attributed to phycocyanin (549 and 619 nm) and phycoerythrin (543 nm) respectively. This has been confirmed by spectrophotometry of the pure products and by literature data [33–35]. After 15 min of laser photolysis (see Fig. 4), the absorption band at 619 nm completely disappears and the band at 549 nm decreases

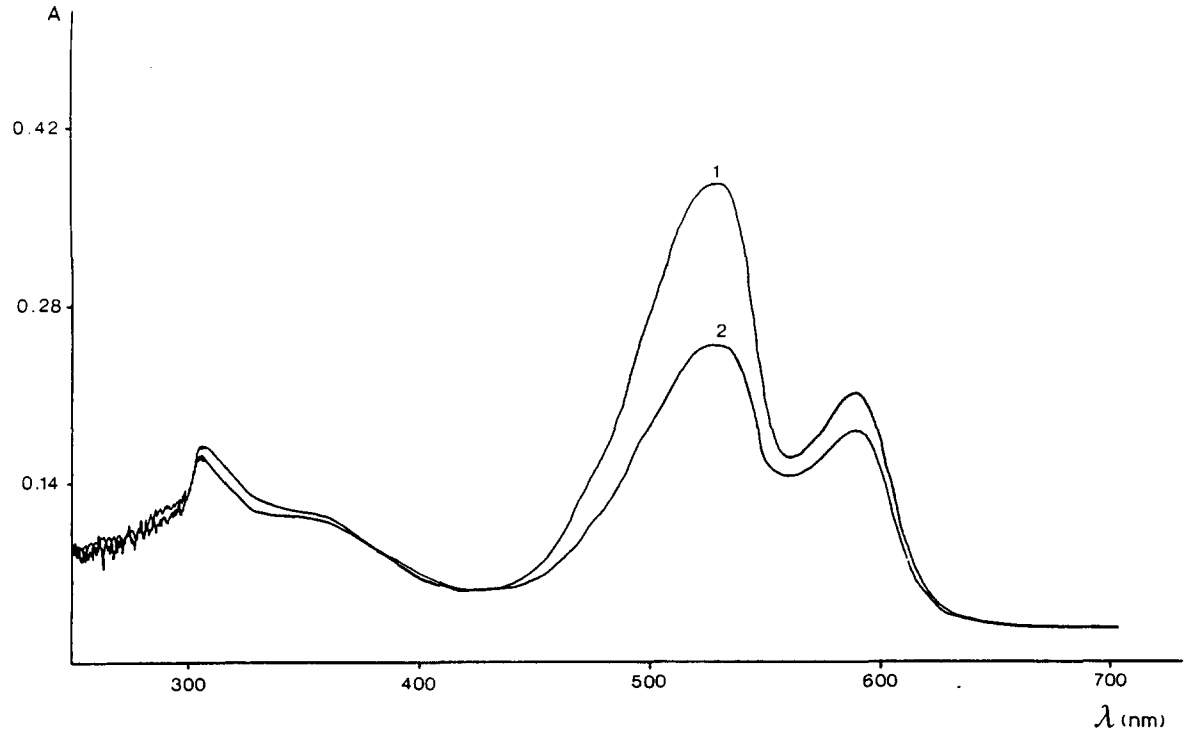


Fig. 5. Absorption spectra of phycobilisomes before (1) and after (2) laser photolysis at 470 nm for phycoerythrin destruction. Laser photolysis time, 10 min; laser repetition rate, 100 Hz; laser intensity, 1 mJ (experiment 8); fivefold dilution in hydrogenphosphate buffer.

Table 2
Laser photolysis of phycobilisomes (for phycoerythrin destruction) as a function of laser wavelength, time and intensity

Experiment[a]	$\lambda_{photolysis}$ (nm)	Time[b] (min)	Intensity (mJ)	$A_{620\ nm}$/ % PC destroyed	$A_{545\ nm}$/ % PE destroyed	α_S
0	–	0	–	0.7/0	0.76/0	–
1	490	5	1	0.48/31	0.40/63	2
2	490	10	1	0.40/43	0.30/78	1.8
3	490	13	1	0.34/51	0.25/83	1.6
4	490	5	2.5	0.45/32	0.34/62	1.9
5	490	5	15	0.23/67	0.22/74	1.1
6	480	5	1	0.56/20	0.51/46	2.3
7	480	10	1	4.48/31	0.37/71	2.3
8	470	10	1	0.5/29	0.40/66	2.4

[a]Fivefold dilution in hydrogenphosphate buffer.
[b]Laser repetition rate, 100 Hz. PE, phycoerythrin; PC, phycocyarin.

to 20%, which is exactly the contribution of phycocyanin at this wavelength. These results were confirmed by GC. This destruction can also be followed directly since the colour of the solution changes from red to bright pink. It is important to note in this particular laser photolysis experiment that, despite the fact that phycoerythrin and phycocyanin are very close in terms of their chemical formulae, and a very high density of energy is focused into the solution, only phycocyanin is eliminated.

Selective elimination of phycoerythrin without destruction of phycocyanin is more difficult since the latter (absorption maximum at 549 nm) has an important absorption contribution at 543 nm. However, by using a laser wavelength shifted to 490 nm and lower wavelengths, at which phycoerythrin still has a high absorption coefficient and phycocyanin has a much smaller absorption coefficient than at 543 nm, it was possible to perform selective elimination. Fig. 5 shows the absorption spectra obtained before and after laser photolysis at 470 nm; as expected phycoerythrin is eliminated but phycocyanin is also partially eliminated. Table 2 presents the results obtained for this destruction as a function of the laser wavelength, intensity and time. For comparison purposes, a selectivity coefficient (α_s) was defined as

α_s = (% PE destroyed)/(% PC destroyed)

These percentages were calculated from the absorption measurements. The higher α_s, the more selective the destruction. From this table, several comments should be made: first, at constant wavelength, the longer the laser photolysis time (experiments 1–3), the lower α_s; however, this phenomenon must be clarified since it is not always true (experiments 5 and 6); secondly, an increase in intensity for the same photolysis time leads to a decrease in α_s (experiments 1, 4 and 5), which shows the importance of optimizing the intensity to control multiphoton processes; finally, as the photolysis laser wavelength is shifted to lower values, α_s increases (experiments 6–8), which is related to the fact that the absorption coefficient of phycocyanin becomes very low. From this study, it can be seen that it is possible to destroy more than twice as much phycoerythrin than phycocyanin (experiment 8) with short-time laser photolysis (10 min), low intensity (1 mJ) and a shifted photolysis laser wavelength (470 nm) (compared with the maximum absorption wavelength of 543 nm).

4. Conclusions

Laser photolysis has been successfully applied to the destruction of several molecules in complex essential oils as well as for the purification of a biocompatible dye. In most cases, the products formed are of lower molecular weight than the initial compounds and are likely to present no noxiousness. This process, complementary to other existing techniques, may be of great interest for high added value products, especially in the pharmaceutical industry for last step purification. Laser parameters (wavelength, intensity and photolysis time) must be adapted to each specific case to achieve maximum destruction with minimum side products. However, in each case, the non-toxicity of the products formed must be tested before application.

References

[1] J.G. Calvert and J.N. Pitts, Jr., in *Photochemistry*, Wiley, 1966.
[2] J.C. André, A.B. Vannes and R. Plancher, in Electra (ed.), *Techniques d'Utilisation des Photons: Principes et Applications*, DOPEE Diffusion, 1992.
[3] V.S. Letokhov, *Physics Today, 33* (1980) 34.
[4] R.M. Wilson and K.A. Schnapp, *Chem Rev., 93* (1993) 223.
[5] A. Tsuchida, M. Yamamoto and Y. Nishijima, *Bull. Chem. Soc. Jpn., 64* (1991) 3402.
[6] O.I. Kovalsky and E.I. Budowski, *Photochem. Photobiol., 51* (1990) 659.
[7] A. Marshall, A. Clark, R. Jennings, K.W.D. Ledingham and R.P. Singhal, *Int. J. Mass Spectrom. Ion Processes, 112* (1992) 273.
[8] S.A. Rogers and S.R Leone, *Appl. Spectrom., 47* (1993) 1430.
[9] G. Beddar, *Mol. Photophys., 56* (1993) 63.
[10] R.V. Ambartzumanian, *Kvantovaya Elektron., 4* (1977) 171.
[11] J.H. Clark and R.G. Anderson, *Appl. Phys. Lett., 32* (1978) 46.
[12] R.H. Eastmann and A.V. Winn, *J. Org. Chem., 28* (1963) 2162.
[13] R.S. Cook and G.D. Lyon, *J. Am. Chem. Soc., 103* (1981) 7317.
[14] W.A. Noyes Jr., G.S. Hammond and J.N. Pitts Jr., *Advances in Photochemistry, Photochemistry of the Cyclic Ketones*, Vol. 1, Wiley Interscience, New York, 1963.
[15] J. March, *Advanced Organic Chemistry, Reactions, Mechanism and Structure*, McGraw-Hill, New York, 2nd edn., 1977.
[16] R.O. Kan, *Organic Photochemistry, Reactions Through Bond Dissociation*, McGraw-Hill, New York, 1966.
[17] J.F. Thorpe and M.A. Whitely, Thorpe's Dictionary of Applied Chemistry, Vol. 1, Lowe and Brydone, 1937, p. 683, Vol. 8, Lowe and Brydone, 1947, p. 655.
[18] H.H. Wisneski, *J. Assoc. Anal. Chem., 59* (3) (1976) 547.
[19] M.W. Mantulin and P.S. Song, *J. Am. Chem. Soc., 95* (1973) 5122.
[20] N. Mazzuli and H. Maiback, *J. Soc. Cosmet. Chem., 21* (1970) 695.
[21] M.E. Perel'son, A.I. Ban'kovskii and A.A. Kir'yanov, *Khim. Prir. Soedin., 2* (6) (1966) 381.
[22] T.A. Moore, M.L. Harter and P.S. Song, *J. Mol. Spectrosc., 40* (1971) 144.
[23] K.H. Lee and T.O. Soine, *J. Pharm. Sci., 58* (1969) 681.
[24] M.A. Whitely, Thorpe's Dictionary of Applied Chemistry, Vol. 8, Lowe and Brydone, 1947, p. 662.
[25] J.F. Thorpe and M.A. Whitely, Thorpe's Dictionary of Applied Chemistry, Vol. 10, Lowe and Brydone, 1950, p. 656.
[26] S. Mihara and T. Shibamoto, *J. Agric. Food. Chem., 30* (6) (1982) 1215.
[27] Z.L.F. Gaibel and L. Fishbein, *Va. J. Sci.*, (1969) 17.
[28] Y.R. Naves and P. Ardizio, *Bull. Soc. Chim. Fr., 24* (1957) 1053.
[29] P. Zoller and R. Brun, *Helv. Chim. Acta, 37* (22) (1954) 196.
[30] R.F. Patterson and H. Hibbert, *J. Am. Chem. Soc., 65* (1943) 1862.
[31] G. Kaupp, O. Sauerland, T. Marquardt and M.J.J. Plagmann, *Photochem. Photobiol. A: Chem., 56* (1991) 381.
[32] E. Gantt and C.A. Lipschultz, *Biochim. Biophys. Acta, 292* (1973) 858.
[33] E. Gantt and C.A. Lipschultz, *Biochemistry, 13* (14) (1974) 2960.
[34] E. Fujimori and J. Pecci, *Arch. Biochem. Biophys., 118* (1967) 448.
[35] F.W. Teale and R.E. Dale, *Biochemistry, 116* (1970) 161.