Coke formation during the reaction was determined by heating the catalyst at 500°C for 6 h in a current of air. The carbon dioxide evolved was absorbed in a known volume of the standard barium hydroxide solution. The barium carbonate formed was separated quantitatively. After drying it was weighed. The weight of carbon was determined gravimetrically. The unreacted barium hydroxide solution was titrated against hydrochloric acid. From this the weight of coke on catalyst was determined volumetrically also. Coke formation was maximum on Ce–Y catalyst. The acidity of the cerium form of zeolite is higher than that of H and Na forms. It is observed that the formation of coke from the amines is more on more acidic forms of zeolite.

N-benzylethanolamine reacts over Y and ZSM-5 zeolites at 350–450°C to yield a variety of products, including imines formed by dehydration, products formed by reaction with the solvent benzene and 1,2-diphenylethane. However, the expected cyclodehydration could not be achieved.

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Production of singlet oxygen by sanguinarine and berberine

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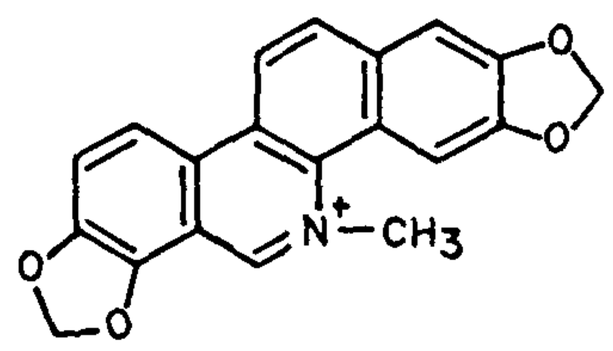
Production of singlet oxygen by sanguinarine and berberine has been studied from absorption spectroscopy measurements using dimethylfuran as the singlet oxygen acceptor. Comparative spectroscopic studies show that the rate of singlet oxygen generation of sanguinarine is higher than that of berberine.

ALKALOIDS occupy an important position in applied chemistry and play an indispensable role in medicinal chemistry. Alkaloids with fused aromatic rings have the potential to form a molecular complex with DNA and are of particular interest because they exhibit a broad range of biological activities[1–6]. Sanguinarine (Structure I, Figure 1) is a benzophenanthridine alkaloid while berberine (Structure II, Figure 1) is a benzodioxolobenzoquinolizine alkaloid. Both compounds have been reported to possess antitumour, antimicrobial and various other biological properties[5,6]. It has been shown that both compounds bind to DNA by a mechanism of intercalation[7–13]. Recently, a large number of biologically active compounds, some of them accepted to be potent drugs, have been found to produce singlet oxygen – an excited form of molecular oxygen that is involved in many photosensitized biological activities[14–22]. In this communication we describe our attempts to demonstrate the production of singlet oxygen by sanguinarine and berberine from absorption spectroscopy measurements.

Sanguinarine chloride and berberine chloride were purchased from Aldrich Chemical Co., St. Louis, MO, USA, and Sigma Chemical Co., St. Louis, MO, USA, respectively, and were used after checking their purity



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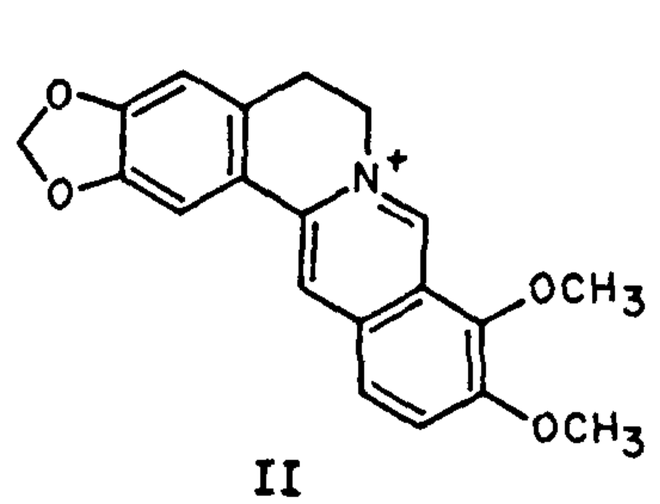

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Figure 1. *Chemical structures of sanguinarine (structure I) and berberine (structure II).*

*For correspondence.

by thin-layer chromatography, and then by NMR, UV absorption and fluorescence emission. Both the compounds are highly soluble in distilled water. The concentration in the aqueous solution was measured using an extinction coefficient (ε) of 24, 271 M^{-1} cm^{-1} at 327 nm for sanguinarine, and of 22, 500 M^{-1} cm^{-1} at 344 nm for berberine. Dimethylfuran (DMF) of analytical grade was obtained from Sigma Chemical Co., St. Louis, Mo, USA. All other reagents used were of analytical grade. Deionized distilled water was used throughout. Experiments were carried out in CP buffer (0.00466 M citric acid and 0.01068 M disodium phosphate) pH 5.2. The solution pH was measured in a PH M84 research pH meter (Radiometer, Copenhagen, Denmark) with an accuracy of 0.005.

Singlet oxygen ($^1O_2$) production was detected using DMF as the singlet oxygen acceptor as described earlier[17]. Briefly, 1 ml of sanguinarine (13.8 μM) or berberine (13.8 μM) was added to 0.05 μl/ml DMF in 1 cm quartz cuvettes which were sealed with teflon stoppers. The compounds were irradiated for different time intervals at 330 nm (for sanguinarine) and 350 nm (for berberine) with light obtained from a 400 W high-pressure Hg lamp using a Jarrel Ash 0.25 m monochromator with fully opened entrance and exit slits. The intensity of radiation incident on the sample was found to be 1.52×10^{16} quantas/s and 1.44×10^{16} quantas/s at 330 nm and 350 nm, respectively[19]. Absorption spectra of sanguinarine or berberine in DMF were recorded on a Beckman Model-24 spectrophotometer against a reference sample in a 1 cm cuvette after being exposed to the light for different times. Singlet oxygen generation was monitored from the decrease in absorbance of DMF at 220 nm, which was consumed in the reaction with $^1O_2$. The controls included direct irradiation of DMF without the sensitizer. The above experiments were performed at 22°C. We can generalize the singlet oxygen production scheme as follows:

$$M \xrightarrow{h\nu} M^* + {}^3O_2 \rightarrow M + {}^1O_2,$$

where M and M^* represent the ground state and excited triplet state of sanguinarine and berberine molecule, respectively.

The UV–visible absorption of sanguinarine in CP buffer is characterized by three maxima centered at 273, 327 and 468 nm, while that of berberine at 227, 262, 344 and 420 nm in the wavelength range 200–700 nm. The absorption spectrum of DMF in the same buffer has only one maximum centered at 220 nm in the wavelength range 200–250 nm and, thereafter, it does not produce any spectral pattern up to 700 nm. When sanguinarine or berberine was exposed to light for a period of 1 h, it has been observed that with or without irradiation the spectral pattern of each alkaloid is superimposable. This result indicates that none of the alkaloids is affected by irradiation. Figure 2 shows some representative spectra of the sanguinarine–DMF mixture at different time intervals after exposure to light at 330 nm. It can be seen that the decrease in intensity at 220 nm increases with increasing time of light exposure due to the consumption of $^1O_2$ generated by sanguinarine at different time intervals. A similar decrease in absorption intensity at 220 nm was also observed in the presence of berberine. In order to check the involvement of triplet-state oxygen in the reaction mixture, nitrogen gas was bubbled for 30 min prior to and also during irradiation. The results showed that under nitrogen bubbling no detectable change of absorption pattern of the sanguinarine–DMF mixture (Curve 1) was observed. This clearly shows that in the absence of oxygen in the mixture, the production of $^1O_2$ was stopped. It is known that DMF reacts with $^1O_2$ through the formation of its peroxide compound[17,20]. Again, spectral patterns (Figure 2) are always superimposable in the wavelength range 300–350 nm, with maximum at 327 nm, which is the maximum for sanguinarine, indicating that the quantity of sanguinarine before and after irradiation is the same and sanguinarine does not react with $^1O_2$.

The kinetics of decrease in the absorbance of DMF at 220 nm due to the consumption of $^1O_2$ generated by sanguinarine or berberine at different time intervals are shown in Figure 3. It can be seen from Figure 3 that a 50% decrease in absorption occurred within 19 min for sanguinarine and 78 min for berberine. The rate of

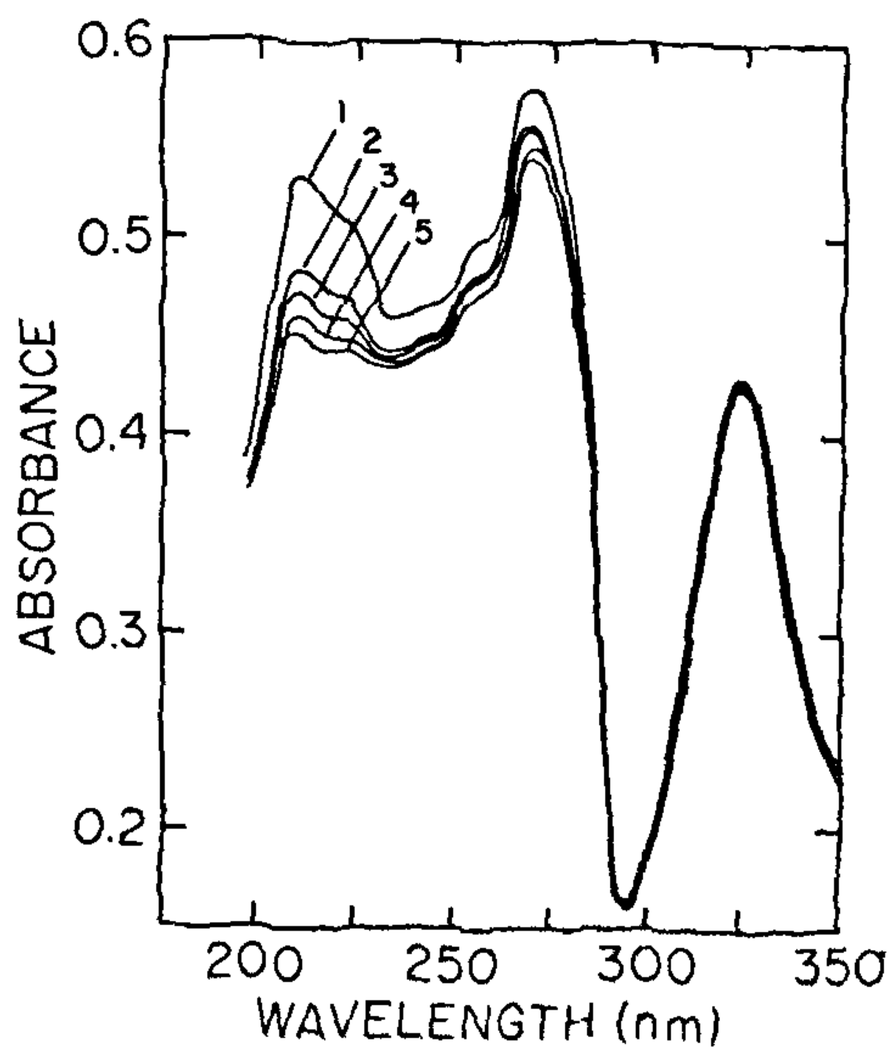

Figure 2. Effect of irradiation at 330 nm for different time intervals on the absorption spectrum of the sanguinarine–DMF mixture in CP buffer, pH 5.2. Curves 1–5 denote the time of exposure for 0, 25,

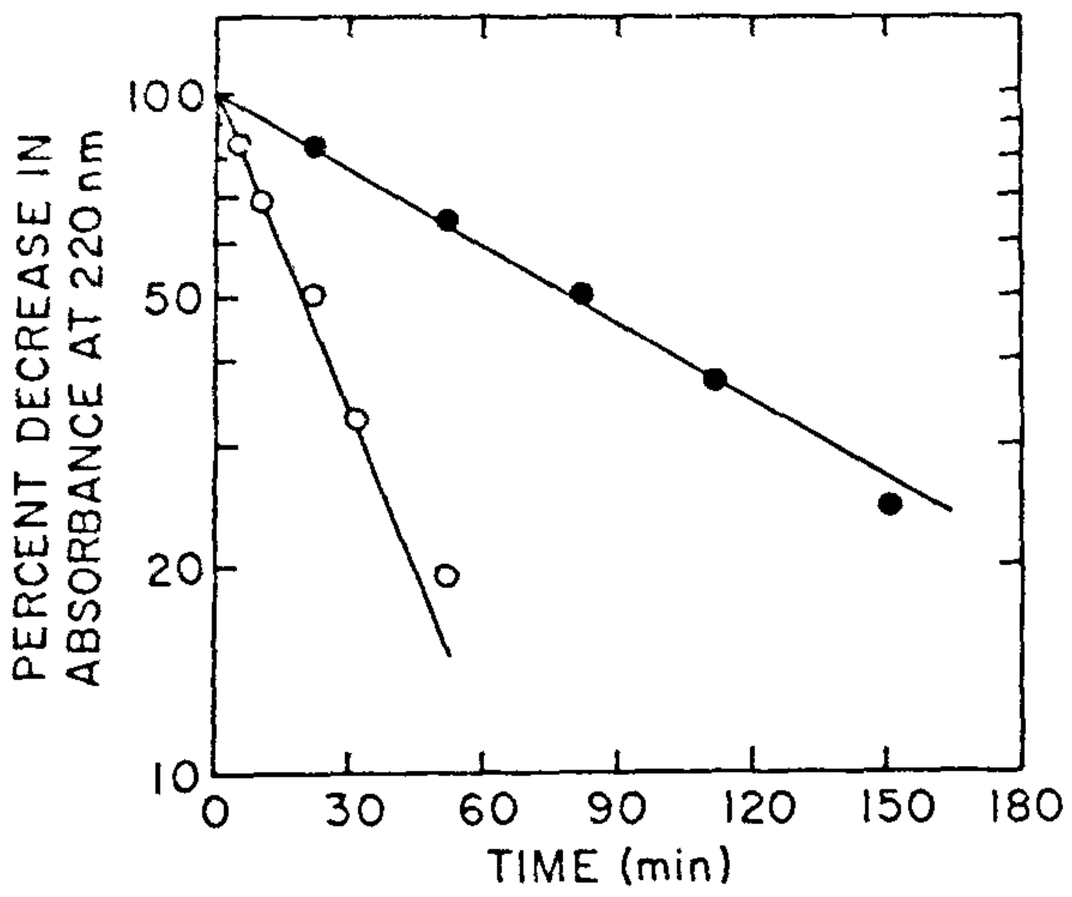

Figure 3. A plot of percentage decrease of absorbance of DMF at 220 nm versus time of exposure· O—O, for sanguinarine and ●—●, for berberine. The percentage decrease of absorbance was calculated after subtracting the absorbance intensity at 220 nm for each sensitizer. Sanguinarine (13.8 μM) was irradiated at 330 nm, while berberine (13 8 μM) was irradiated at 350 nm.

$^1O_2$ generation was found to be $6.075 \times 10^{-4}\ s^{-1}$ and $1.462 \times 10^{-4}\ s^{-1}$ for sanguinarine and berberine, respectively. The efficiency of $^1O_2$ production by sanguinarine is four times higher than berberine but comparable to harmine[20]. In this context, it is pertinent to point out that berberine (Structure II, Figure 1) has a partial saturation in the chemical structure and, in contrast to sanguinarine (structure I, Figure 1), has a planar and aromatic ring system like ethidium. The observed differences in the varying efficiencies of $^1O_2$ production by the two alkaloids in solution may be rationalized on the basis of their structural differences.

Several classes of tricyclic alkaloids have been shown to be toxic to a variety of organisms in the presence of light, including some furanoquinolines, β-carbolines[20]. It is known that intercalating complexes of sanguinarine–DNA or berberine–DNA are important in their antitumour and other biological activities[5,6] even without exposure to light. Thus, in the presence of light both the alkaloids may have greater effectiveness towards their biological activities.

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Turbulent drag reduction by polymer-based mixtures and graft copolymers

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Ever since the discovery of turbulent drag reduction phenomenon, the search for materials with drag reduction effectiveness and shear stability is continuing. Polymers, soaps, fibres and their mixtures have been found to be effective drag reducers. The polymer–polymer and polymer–fibre mixtures have extensively been studied in the author's laboratory in recent years. Synergistic combinations of polymer–polymer and polymer–fibre mixtures which provide high drag reduction effectiveness and shear stability have been found. It has been shown in the author's laboratory by extensive grafting of polyacrylamide chains on to the backbones of guargum, xanthangum and carboxymethylcellulose as well as polymers like poly(vinyl alcohol) and low molecular compound starch that it is possible to develop graft copolymers which have high drag reduction effectiveness like