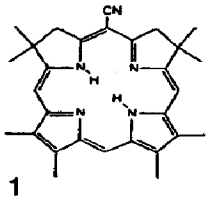
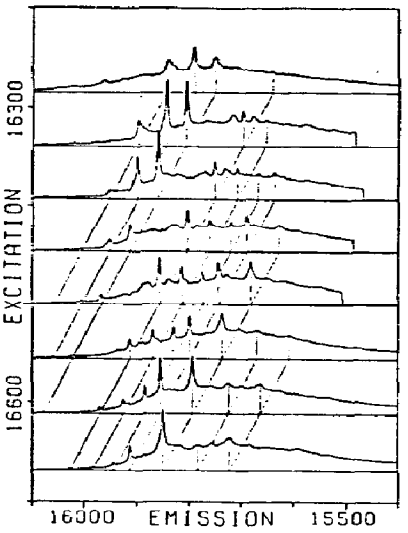
$S_1 \leftarrow S_0$ energy with a narrow-band laser, however, results in well-structured and excitation-wavelength-dependent emission spectra. It is shown that a site selection effect is responsible for this behaviour.

A set of fluorescence spectra of isobacteriochlorin in 3-methylpentane at 4.2 K excited at eight different frequencies is shown. We note that the line pattern varies enormously from one spectrum to another. A comparison of two spectra taken at random would hardly indicate that they result from the same compound.



1



Photochemical and photobiological properties of haematoporphyrin derivatives

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Derivatives of haematoporphyrin (HpD) have been introduced in the diagnosis and therapy of cancer because of their selective retention in tumours, their characteristic fluorescence and their efficiency as photosensitizers. We analysed HpD with respect to (a) chemical composition, (b) cellular uptake of the components, (c) relative efficiency of the components in sensitizing photoinactivation of cancer cells, (d) fluorescence spectra and fluorescence quantum yields and (e) quantum yields of singlet oxygen production. The major components of HpD, as analysed by high pressure liquid chromatography, are (listed in order of decreasing water solubility) (1) two stereoisomers of haematoporphyrin, (2) two stereoisomers of each of two positional isomers of *o*-acetyl

haematoporphyrin, (3) the isomers 2(4)-1-hydroxyethyl-4(2)vinyl deuteroporphyrin, (4) two stereoisomers of *o,o'*-diacetyl haematoporphyrin, (5) two positional isomers of 2(4)-*o*-acetyl-4(2)vinyl deuteroporphyrin and (6) components with elution properties that are similar to those of protoporphyrin. In aqueous solution at pH $\approx$ 7, only three ((1), (3) and (6)) of these major components are stable. Cellular uptake, efficiency as photosensitizers and binding to serum proteins increase in the mentioned order. Further data are presented.

Comparative study of the primary events in the photolysis of hemoglobin systems by picosecond absorption spectroscopy

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Research involving the photolysis of six-coordinate Fe(II)–CO and Fe(II)–O_2 complexes of hemoglobin (Hb) and myoglobin (Mb) has been a subject of intense interest ever since Gibson's [1] initial description of the photoinitiated recombination kinetics of CO with deoxyHb and Mb. The primary reason for interest in this research area is derived from the ability to interrogate the dynamics of re-ligation of photolyzed heme optically in various time frames, ranging from picosecond to millisecond, in order to gain insight into the cooperative binding of O_2 to Hb. In this context we wish to discuss our most recent picosecond photodissociation experiments on solutions at 5 °C of the O_2, CO and NO derivatives of Mb, Hb and certain synthetic analogues.

In our presentation we place emphasis on the comparative aspects of the dynamics of the intial or primary stages of photolysis and geminate recombination of these molecules, as determined by their transient photoproduct absorption spectra.

1 Q.H. Gibson, *J. Physiol., 134* (1956) 112 - 122, 123 - 124.