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SYNTHESIS AND SPECTRAL PROPERTIES OF ZINC PORPHYRINS HAVING AMINO ACID RESIDUES

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Mesoporphyrin-IX monomethyl ester (1), consisting of two geometrical isomers, was converted into acyl chloride,which was reacted with aromatic amino acid monomethyl esters like L-Phe-OMe, L-Tyr-OMe, L-Trp-OMe, and N^{im}-Bzl-His-OMe, followed by treatment with zinc acetate to give zinc complexes (2a, 2b, 2c, and 2d) of the corresponding porphyrin monomethyl ester linked with amino acid residues by amide bonding. Tyramine was combined with 1 through amide bonding in the same manner to yield zinc complex of N-[2-(p-hydroxyphenyl)ethyl]amide of 1 (2e).

The characteristic features of the visible spectra of the zinc complexes can be divided into three groups; 1) no effect of amino acid residue of 2a and 2c, 2) the red shift due to intramolecular ligand, imidazole, in 2d, and 3) the blue shift of the Soret band in 2b and 2e due to the dimer formation. The behavior of 2b and 2e is remarkable, since the dimer formation was observed even in highly diluted solution in toluene (ca. 10^{-6} M/l).

The NMR-spectra of 2b, in particular the meso-protons, were found to be almost insensitive to the concentration (0.02-0.09 M/l) in $CDCl_3$, whereas the meso-protons of 2a, 2c, and 2d demonstrated the concentration dependence. The facts was interpreted in terms of the complete dimer formation of 2b in the measurement conditions.

The ester C=O of 2b in the ir spectrum in CH_2Cl_2 was split into two peaks at 1739 and 1721 cm^{-1}, while ν_{CO} of 2a, 2c and 2d were at ca. 1736 cm^{-1}. 2e, which has no methyl ester group derived from amino acid ester, showed hydrogen-bonded frequencies both ester and amide groups. The results revealed that there are two kinds of two hydrogen bondings between -CONH...O=C-OMe and -HNCO...HOØ-. The structure for the dimer was proposed, based on these results.

Aromatic amino acid residues demonstrated no influence on the fluorescence spectra of zinc porphyrin nucleus, excluding the case of 2d which undergoes red shift owing to the intramolecular ligand. Furthermore, fluorescnece quenching experiments were carried out, using oxygen and α-cyanostilbene as quenchers.