SYNTHESES OF 1,5-DI(CARBOXYETHYL)-2,6-DIMETHYL-3,4,7,8-TETRAETHYL-PORPHIN AND ITS DERIVATIVES

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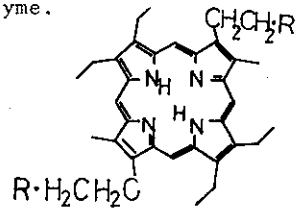
Syntheses of 1,5-di(carboxyethyl)-2,6-dimethyl-3,4,7,8-tetraethylporphin and its derivatives are described and their spectroscopic properties are discussed.

Dipyrromethene 3 was prepared by the condensation of 2,3-dimethyl-4-[2-carboxyethyl]-pyrrole 1 and 3,4-diethyl-2-formylpyrrole 2. Treatment of 3 with bromine afforded 5-bromo-5'-bromomethyl-dipyrromethene 4. Coupling of 4 with 3 in the presence of stannic chloride gave a,c-biladiene hydrobromide 5. Thus obtained 5 was cyclized to 1,5-di(carboxyethyl)2,6-dimethyl-3,4,7,8-tetraethyl-porphin 6. The porphyrin 6 was purified as 1,5-dimethylester-porphyrin derivative 7. The dimethylester was reduced to 1,5-(hydroxyethyl)-porphyrin 9 derivative by using $LiAlH_4$ in tetrahydrofuran. Condensation of 7 with n-butylamine was performed through 1,5-di(chloroformylethyl)-porphyrin. When dicyclohexylcarbodiimide (DCC) was used as a condensation reagent, the reaction of 7 with amine was unsuccessful to give the product 11 condensed with DCC. Their structure were confirmed by microanalyses and spectroscopic properties. The porphyrin 7 may provide us an accessible route to construct a model of heme enzyme.



R = CO_2Et 6
CO_2H 7
CH_2OH 9
$CONHCH_2CH_2CH_2CH_3$ 10
CON-CONH 11