

Title	Porphyrins with metal-chelating groups in the peripheral region
Sub Title	
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Publisher	共立薬科大学
Publication year	1987
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.32 (1987.) ,p.112- 113
JaLC DOI	
Abstract	
Notes	学会講演要旨
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000032-0118

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HPLC Analysis of Ginsenosides in *Panax ginseng* Extracts Using Glass-ODS Column

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[11th International Symposium on Column Liquid Chromatography
(1987年7月, Amsterdam, The Netherlands) で発表]

The paper is concerned with a high performance liquid chromatographic (HPLC) method using a column of octadecylsilil (ODS) porous glass for separation and quantitative determination of ginsenosides in *Panax ginseng* extracts and in pharmaceutical preparations.

Acetonitril-water was used as the mobile-phase. The retention times of ginsenosides were greatly affected by the water content of the mobile phase. Ginsenosides Rb₁, Rb₂, Rc, Rd, Rf and Rg₂ were separated with acetonitrile-water (27.5 : 72.5) with a flow-rate of 1 ml/min. Also a well-resoluted chromatogram of ginsenosides Re, Rg₁ and Ro was obtained with acetonitrile-water (16.5 : 83.5) with a flow-rate of 1 ml/min. The whole separation was achieved in 12 min. The calibration curve of each ginsenoside has a correlation coefficient very near to unity.

The rapid and accurate analysis of ginsenosides is possible by the present method.

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Porphyrins with Metal-chelating Groups in the Peripheral Region*

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[3rd International Conference on Bioinorganic Chemistry,
(1987年7月, Noordwikerhout, The Netherlands) で発表]

A porphyrin with metal-chelating groups in the peripheral region is expected to find wide application in medical and analytical sciences. As models of such porphyrins, we prepared *meso*-tetra[5-(8-hydroxyquinoly)]porphine and one of its isomer, *meso*-tetra[2-(8-hydroxyquinoly)]porphine.

The porphyrins are represented by $\text{PH}_2(\text{QOH})_4$, where PH_2 stands for the porphine moiety with two pyrrole hydrogens, and QOH for the quinolinol moiety. Three kinds of metal complexes are possible for the porphyrins. These are free base porphyrin with metal chelated 8-quinolinol group ($\text{PH}_2(\text{QOM})_4$), metalloporphyrin with unchelated quinolinol ($\text{PM}(\text{QOM})_4$) and metalloporphyrin with metal chelated quinolinol ($\text{PM}(\text{QOM})_4$),

where M indicates a metal ion.

The porphyrins were soluble in dimethylformamide (DMF) but practically insoluble in water. The DMF solutions showed the spectra characteristic of the free base porphyrin with the Soret band and the four weak visible bands. Addition of Cu(II) perchlorate to the solution resulted in biphasic spectral changes, an instantaneous change and a subsequent slow change. The latter change was observable at room temperature only under a large excess of Cu(II) over the porphyrin. The spectra after the completion of the first step were ascribed to the formation of $\text{PH}_2(\text{QOCu}^+)_4$. In the spectra after the completion of the second slow step, the four visible bands were replaced by two band characteristic of metalloporphyrin and the change should indicate the formation of $\text{PCu}(\text{QOCu}^+)_4$.

The kinetics of the second step in DMF were measured at 30° by monitoring the absorption at around 523 nm. The formation of the metalloporphyrin followed the first order kinetics under a large excess of Cu(II). The observed first order rate constant, k_0 , increased linearly with the increase of the total concentration of Cu(II). The values of the second order rate constants were 0.92 and 0.41 $\text{M}^{-1}\text{sec}^{-1}$ for the 2- and 5-isomers, respectively.

The addition of HClO_4 to the $\text{PCu}(\text{QOCu}^+)_4$ solution gave rise to the spectra assignable to $\text{PCu}(\text{QOH})_4$, in which the two weak visible bands characteristic of the metalloporphyrin spectrum were blue shifted. The decrease of the absorbance of the Soret band along with the metal chelation of the quinolinol moiety was noted.

* 発表の要旨は *Rec. Trav. Chim.*, 106, 333 (1987) に掲載.

ピリドキサール酵素のモデル

松島美一

〔日本薬学会九州支部第4回研修会(1987年7月, 福岡)における特別講演〕

酵素モデルの代表的研究と言われるピリドキサール酵素のモデルについて, その酵素の理解に果たしてきた役割を概説した。錯体化学の貢献, 反応モデルから分光学的モデルへの変容, 準安定中間体のモデル, 最近のトピックについても論じた。