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Synthesis and Chromogenic Properties of New Water-Soluble Glycosylated Porphines

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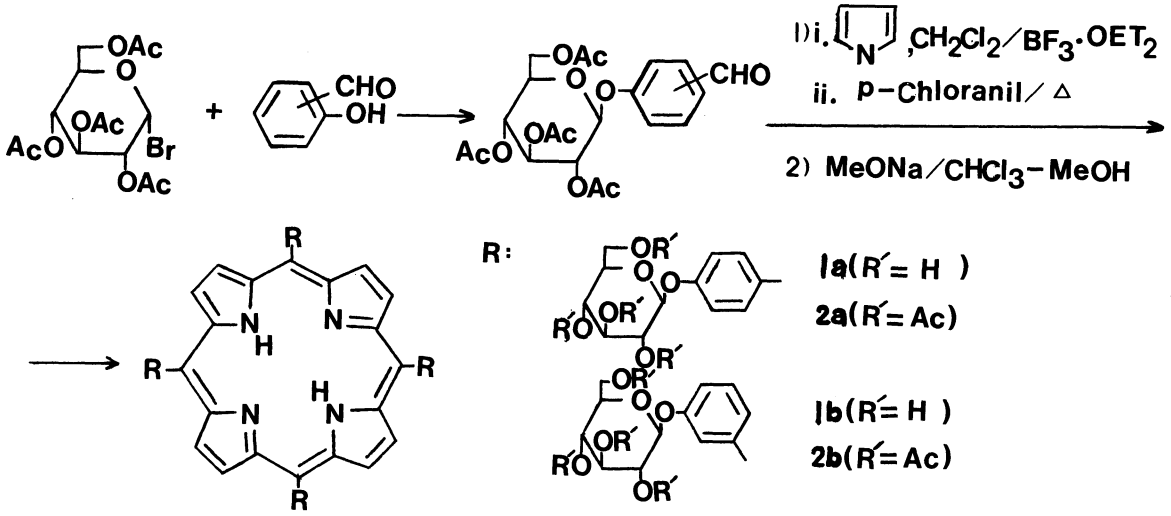
We synthesized two kinds of new water-soluble glycosylated porphines, 5,10,15,20-tetrakis[4′-(β-D-glucopyranosyl)phenyl] porphine and 5,10,15,20-tetrakis[3′-(β-D-glucopyranosyl) phenyl] porphine, and investigated their chromogenic properties and reactivities with copper(II) ion.

In recent years water-soluble *meso*-substituted porphines have been extensively studied as a highly sensitive spectrophotometric reagent for metal ions having very large molar absorptivity (ε= 2 - 6 x $10^5 mol^{-1}dm^3cm^{-1}$, at 400 - 500 nm).[1] Every water-soluble porphine so far prepared has been a cationic, anionic or amphoteric ion type.[2] Previously we developed a water-soluble glycosylated hydrazone, bis(D-glucose)oxalyldihydrazone, and used it for the spectrophotometric determination of copper.[3] Based on these backgrounds we directed the attention to the high water-solubility of sugars and synthesized two kinds of neutral type of glycosylated porphines, which had β-D-glucopyranose moiety at the *para*- or *meta*-position of *meso*-substituted benzene



Scheme 1.

ring. Recently P. Maillard *et al.* reported 5,10,15,20-tetrakis[2'-(β-D-glucopyranosyl)phenyl]porphine as a superstructured model of active site of hemoprotein, but did not referred to the spectroscopic characteristics. [4] This *ortho*-substituted porphine is not useful as a spectrophotometric reagent because it consists of three atropisomers and it is very tedious and time-consuming to separate each other.

In this report we synthesized *para*- and *meta*-substituted porphines which did not contain any atropisomers, elucidated their chromogenic properties and investigated their applications in analytical chemistry.

Scheme shows the procedure for the synthesis of glycosylated porphines. As for the condensation of glucopyranosylbenzaldehyde[5] with pyrrole we employed Lindsey's method which gave the target porphine in higher yield without difficult purification problems.[6,7] We could get target porphines in reasonable high yields(**2a**:53%, **2b**:20.3%), which were identified by ^{1}H-NMR, FABMS and elementary analysis.[8] Fig. 1 shows the ^{1}H-NMR spectra of **2a** and **2b**. They were converted to free glycosylated porphines(**1a** and **1b**) by a catalytic amount of sodium methanolate in dry chloroform-methanol(1+1, v/v) and also identified by ^{1}H-NMR, FABMS and elementary analysis.[9] The detailed procedure for the synthesis will be described elsewhere.

Porphines **1a** and **1b** are soluble in water and ethanol, specially very soluble in a small percentage of ethanol or 1,4-dioxane in water. They are very stable in neutral solution, but are gradually hydrolyzed below pH 1.0. Because of neutral type of porphines they did not show any adsorption on the surface of glassware, or any aggregation over its concentration range up to 10^{-4}mol dm^{-3}.

Spectral data of **1a** and **1b** were summarized in Table 1. They showed typical absorption spectra of meso-substituted porphines, and their soret bands gave very large molar absorptivities.

Figure 2 shows the spectra of **1a**, **1b**, and their complexes for an example with copper(II) ion. The complexation reaction was complete within a few minutes by using 1.0 cm^3 of 0.5% hydroxylamine hydrochloride solution as an accelerator. After the formation of the complex in neutral solution the pH was lowered to 1.0 to separate the Soret band of porphine from that of its complex. The complex remained stable at

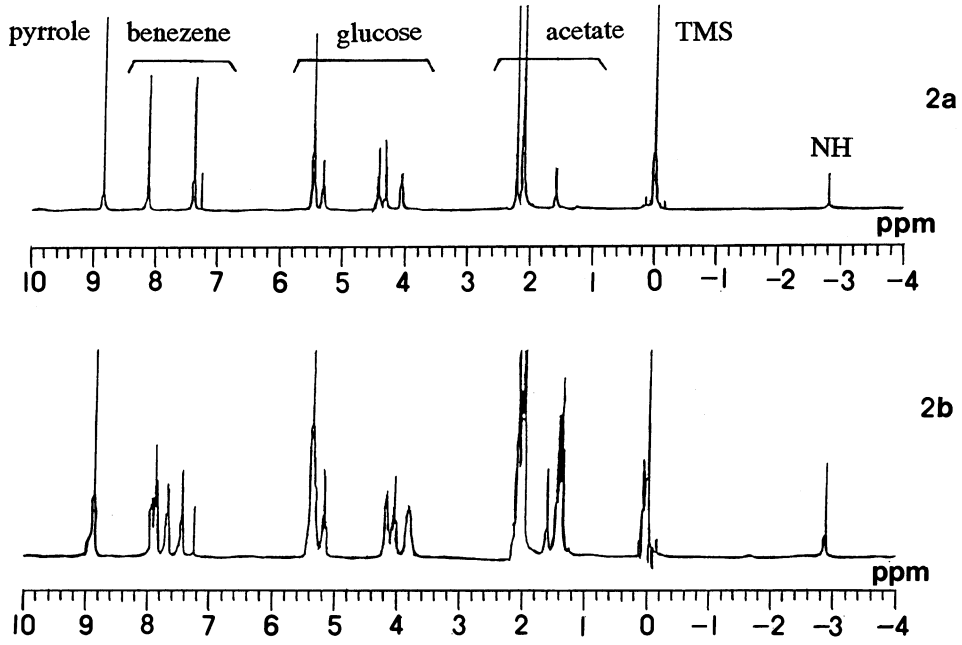


Fig. 1. ^{1}H-NMR(400 MHz) spectra of **2a** and **2b** in $CDCl_3$.

Table 1. Spectral properties of porphines

Porphine	$\lambda max^{a)}$ / nm, $\varepsilon^{b)}$ / $10^4 mol^{-1} dm^3 cm^{-1}$								
	H_2L (pH8.0)					H_4L^{2+} (pH1.0)			
	Soret	I	II	III	IV	Soret	I	II	III
1a	418 (38.4)	519 (1.24)	557 (0.85)	589 (0.47)	647 (0.43)	442 (40.7)		613[c)] (0.93)	669 (5.98)
1b	416 (43.0)	516 (1.50)	552 (0.64)	586 (0.49)	641 (0.30)	439 (39.2)	554 (0.29)	598 (0.92)	650 (4.51)

a) I-IV indicate the λmax at visible region.
b) ε: Molar absorptivity.
c) Shoulder.

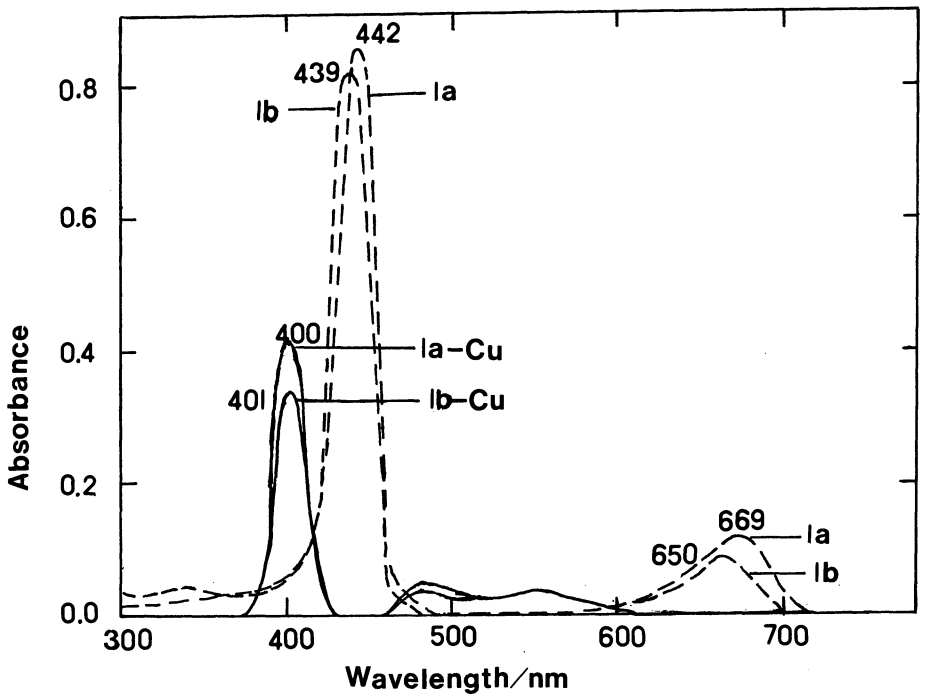


Fig. 2. Absorption spectra. **1a** and **1b**, 2.1 x 10^{-6}M; complexes, 4.2 x 10^{-6}M; pH, 1.0; refernce, water(**1a**, **1b**) and reagent blank (complexes).

this pH value. The ε was not so large as expected(≈1.0 x $10^5 mol^{-1} dm^3 cm^{-1}$). It can be assumed that the steric hindrance of sugar moiety increased in the vicinity of the copper(II) ion. Further studies of other metal complexes are under investigation comparing with the results of ortho-substituted porphines. Studies of new applications of these glycosylated porphines are also under way now.

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8) **2a**: FAB-mass m/z(relative intensity) 2000(100), ^{1}H-NMR($CDCl_3$, TMS), δ-2.8 (2H, s, NH), 2.1-2.3(48H, m, acetate), 4.0-4.5(12H, m, glucose), 7.4 (8H, d, benzene(3′, 5′)), 8.1(8H, d, benezene(2′, 6′)), 8.9(8H, s, pyrrole). Found: C, 59.98; H, 5.09; N, 2.83%. Calcd for $C_{100}H_{102}N_4O_{40}$: C, 60.06; H, 5.14; N, 2.80%. **2b**: FAB-mass m/z(relative intensity) 2000(100), ^{1}H-NMR ($CDCl_3$, TMS), δ-2.9(2H, s, NH), 1.2-1.5(12H, m, acetate), 1.8-2.1(36H, m, acetate), 3.8-4.2(12H, m, glucose), 5.1-5.4(16H, m, glucose), 7.5 (4H, d, benzene(4′)), 7.7(4H, m, benzene(5′)), 7.9-8.0(8H, m, benzene(3′+ 6′)), 8.9(8H, s, pyrrole). Found: C, 59.96; H, 5.00; N, 2.54%. Calcd for $C_{100}H_{102}N_4O_{40}$: C, 60.06; H, 5.14; N, 2.80%.
9) **1a**: FAB-mass m/z(relative intensity) 1327(84), 1328(100), 1329(81), ^{1}H-NMR(DMSO-d6, TMS), δ-2.9(2H, s, NH), 3.3-5.5(glucose), 7.5(8H, d, benzene(3′, 5′)), 8.1(8H, d, benzene(2′, 6′)), 8.9(8H, s, pyrrole). Found: C, 59.92; H, 5.34; N, 4.08%. Calcd for $C_{68}H_{70}N_4O_{24}\cdot 2H_2O$: C, 59.91; H, 5.47; N, 4.11%. **1b**: FAB-mass m/z(relative intensity) 1327(87), 1328 (100), 1329(84), ^{1}H-NMR(DMSO-d6, TMS), δ-2.9(2H, s, NH), 3.2-5.4 (glucose), 7.5(4H, d, benzene(4′)), 7.7(4H, m, benzene(5′)), 7.8-7.9(8H, m, benzene(2′+ 6′)), 8.9(8H, d, pyrrole). Found: C, 56.17; H, 5.32; N, 4.02%. Calcd for $C_{68}H_{70}N_4O_{24}\cdot 7H_2O$: C, 56.20; H, 5.83; N, 3.85%.

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