# *A Simple Method for the Preparation of Crystalline* D*-Mannose*

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In the recent studies on the reaction of carbohydrates with boric acid, the present authors have required a large quantity of crystalline D-mannose. This is usually obtained by the hydrolysis of polysaccharides, such as mannan and glucomannan[1].

A better source of the sugar are the corms of *Amorphophallus* konjac, which contain mannose as glucomannan and are commercially available as " Konjac Flour ". According to the previous methods[2] for the preparation of the sugar from this source, D-mannose is isolated in the form of its crystalline phenylhydrazone, purified as easily crystallizable methyl-$\alpha$-D-mannoside, and then the glycoside is hydrolyzed to free sugar. This phenylhydrazone method is quite expensive, and not suitable for preparation on a large scale.

The phenylhydrazone method is based on the unusual low solubility in water of mannose phenylhydrazone. *N*-phenylmannosylamine, like the hydrazone, is insoluble and easily crystallized from an aqueous solution[3]. Moreover, the *N*-glycoside is very easily hydrolyzed under neutral conditions in the presence of formaldehyde or benzaldehyde. The authors have used *N*-phenyl-D-mannosylamine in isolating D-mannose from "Konjac Flour" and made certain improvements for the preparatory purpose of D-mannose.

The "Konjac Flour" has been hydrolyzed with concentrated or with dilute acid solution. The best results bave been obtained by refluxing it in 1 N acid solution. From the acid hydrolysate D-mannose has been isolated as crystalline *N*-phenylmannosylamine, and the *N*-mannoside has been readily hydrolyzed to free sugar in the usual manner[4]. The yield of sugar from this method is nearly equal to that of the phenylhydrazone method.

## Experimental

**Preparation of *N*-Phenyl-D-mannosylamine.**—*Procedure-A.*—One hundred grams of " Konjac Flour " was mixed with 60 ml. of cold 75% sulfuric acid under cooling, allowed to stand overnight at room temperature and then added to 1 liter of water. The diluted solution was refluxed for 6 hr. The solution was neutralized with barium carbonate to pH 4~5 and the precipitate was filtered off. The filtrate was decolorized with active charcoal and concentrated to 100 ml. in vacuo. Aniline (16 ml.) in 100 ml. of ethanol was added to it. The mixture was kept overnight in a refrigerator. The crystals formed were collected and recrystallized from 50% ethanol. Yield 24 g., m.p. 180~181°C. It was identified with an authentic sample[3].

*Procedure-B.*—" Konjac Flour " (100 g.) was suspended in 1 liter of 1 N sulfuric acid and the mixture was boiled for 10 hr. under refluxing. The dark brown solution was neutralized to pH 4~5 with barium carbonate. The *N*-mannoside was obtained as described above. Yield, 33 g.

**Isolation of D-Mannose from *N*-Phenyl-D-mannosylamine.**—Fifty grams of *N*-phenyl-D-mannosylamine was dissolved in water at 60~70°C and 35% formaldehyde (25 ml.) was added to it. A white precipitate was soon deposited. The mixture was allowed to stand for 24 hr. at room temperature. The white resinous substance was removed and the filtrate was evaporated to a thick sirup. The colorless sirup was dissolved in methanol and *n*-propanol (1 : 1) and seeded with $\alpha$-D-mannose. The crystals were separated and recrystallized from ethanol or acetic acid. Yield, 30 g. (85%), m.p. 130~131°C. $[\alpha]_D^{30}$: 28.4° → +13.3° (*c* 3.9, in water).

Found: C, 40.18; H, 6.84. Calcd. for $C_6H_{12}O_6$: C, 40.00; H, 6.71%.

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