THE BENZYL ETHERS OF POLYSACCHARIDES. I.
THE BENZYL ETHERS OF STARCHES OF VARIOUS ORIGINS.

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The preparation of benzyl ethers of mono- and poly-saccharides was first reported by Gomberg and Buchler.(1) Of those, cellulose benzyl ethers have been continually studied and proved to give products of good quality. At present they are manufactured to reply the demand as lacquer constituents. The benzyl ethers of other polysaccharides, however, have scantily been investigated.(2)

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(1) M. Gomberg and C. C. Buchler, *J. Am. Chem. Soc.*, **43** (1921), 1904.

(2) Brit. P., 149320 (1921); Lilienfeld, D.R.P., 360415 (1922); F.P., 534778 (1921); I.G. Farbenindustrie, Austrian P., 12780 (1932).

Gomberg and Buchler reported that, under their experimental conditions, the benzyl ether obtained from potato starch was not identical with that from corn starch in respect of the composition. From potato starch they obtained monobenzyl ether of the composition corresponding to $C_{12}H_{19}O_{10}\cdot C_7H_7$, while from corn starch, dibenzyl ether of the composition corresponding to $C_{12}H_{18}O_{10}\cdot 2C_7H_7$. They do not seem to have made much further studies on these two different ethers: their melting points and solubilities in some organic solvents did not differ much from each other. There is, however, no explanation by those authors on the difference in behaviours of the different kinds of starches. It is interesting that the starches from different origins gave products of different degrees of benzylation under the same conditions. From this point of view we have undertaken the benzylation of starches from various plants, as they are easily accessible in our country.

For the present, the potato starch, corn starch, wheat starch, "Kuzu-ko" (starch powder prepared from the root of *Pueraria triloba*, MAKINO) and "Warabi-ko" (starch prepared from the root of *Pteridium aquilinum*, KUHN, var. *japonicum*, NAKAI) have been brought under investigation.

Alien from the results reported by Gomberg and Buchler, these starches gave exclusively the dibenzyl ethers of the composition corresponding to $C_{12}H_{18}O_{10}\cdot 2C_7H_7$ under our experimental conditions which did not differ much from those mentioned by them. At first our results of elementary analyses of the products corresponded neither to mono- nor to di-benzyl ether of starch, but on strictly desiccating them, the figures obtained were quite identical with those calculated for dibenzyl ether, well within the limit of experimental errors. The melting points of the products were either discordant from those observed by Gomberg and Buchler. Though the melting points of such amorphous substances cannot be generally expected to be very sharp, the discordance was very much remarkable. Of all the products the melting points were found to lie between 165° and 175°. Furthermore we made polarimetrical measurements of the benzyl ethers from various starches, which showed nearly the same rotatory power.

From our experiments, we cannot definitely gainsay the results obtained by Gomberg and Buchler, but there can be some doubtful points there.

Whether our products which we consider to be dibenzyl ethers from the figures of elementary analyses only, are really so, or mixtures of benzyl ethers of different degrees of benzylation, cannot be determined from the results so far obtained. The matter needs further study, and shall be treated in following reports.

Experimental.

(1) **Preparation of Benzyl Starches.** The starch was dried in an air-oven at 80–90° for some hours. To 1 mol (8 g.) of the dried starch, 4.5 mols (9 g.) of 9% caustic soda and 3.5 mols (22 g.) of benzyl chloride were added. They were well blended in a wide-necked conical flask by shaking vigorously; thus a thick, translucent, homogeneously dispersed liquid was obtained which was heated under occasional shaking in a water bath kept at 80–85° about four hours. In the course of one hour and a half a gummy mass separated and after that no remarkable change was observed. The mode of reaction was nearly the same for all the species of starch used.

(2) **Purification of the Products.** The solution was decanted from the gummy mass and the latter was subjected to steam distillation to remove occluded benzyl chloride and some impurities produced during the reaction. The mass did not come to pieces and the trace of the impurities could not be removed in this way. The steam distillation was stopped; the mass in the flask was drained and pulverised in the mortar with the addition of a small quantity of ether to dissolve the impurities. After repeated washing with fresh ether, the powder was dried in the air-oven at 80–90°. The yield is shown in Table 1, that calculated for mono- and di-benzyl ethers being 10.2 g. and 12.4 g. respectively.

Table 1.

Origin of starch	Potato	Corn	Sweet potato	Wheat	"Kuzu"	"Warabi"
Yield of benzyl ether	11.7 g.	11.4 g.	11.2 g.	11.0 g.	11.3 g.	11.2 g.

The crude products were all more or less discoloured to slightly yellow; the discoloration of that from "Warabi" starch was the most remarkable. The product was dissolved in a small quantity of glacial acetic acid and filtered from minute fragments of insoluble matters through a hot funnel. To the filtrate, pure ether sufficient to precipitate the product was added. The supernatant ethereal solution was decanted and the separated white powder was repeatedly washed with fresh ether to remove the trace of acetic acid. The repetition of the procedure seems to give products of no further purity when we judge from the data of elementary analyses and the inspection of the melting points. The product from "Warabi" starch was three times precipitated in this way.

(3) **Elementary Analyses.** The elementary analysis is the only simplest way to determine the degree of benzylation.⁽³⁾ The product was dried in the air-oven at 80–90° until the weight was constant and it was kept in the desiccator. Before analysis, the sample was dried in Abderhalden's desiccating apparatus in vacuo at 110°; the figures (Table 2) given in the columns designated by I were calculated, with the correction of moisture content, from the values obtained with the samples which were not dried in Abderhalden's apparatus. The mean value of the carbon content lies between 60.43 and 60.78% and that of hydrogen between 6.35 and 6.53% and they are well coincident with those calculated for $C_{12}H_{18}O_{10}\cdot 2C_7H_7$ (C, 61.92; H, 6.35%), and not for $C_{12}H_{19}O_{10}\cdot C_7H_7$ (C, 55.07; H, 6.28).

Table 2. Analyses of Benzyl Ethers from

Potato Starch

	H (%)	C (%)	Ash (%)
I	6.44	60.80	—
	6.59	60.79	—
II	6.37	61.48	0.3
	6.51	60.22	—
	6.66	61.01	0.4
	6.60	60.65	—
	6.53	60.52	0.3
Mean	6.53	60.78	0.3

Corn Starch

	H (%)	C (%)	Ash (%)
I	6.49	61.05	—
	6.55	60.88	—
	6.32	60.70	—
II	6.54	61.18	—
	6.26	60.69	—
	6.34	60.15	0.4
Mean	6.42	60.78	0.4

Sweet Potato Starch

	H (%)	C (%)	Ash (%)
I	6.26	59.79	—
	6.45	60.74	—
	6.29	60.64	—
	6.25	60.31	—
II	6.44	60.64	0.4
	6.40	60.37	0.4
	6.37	60.54	—
Mean	6.35	60.43	0.4

Wheat Starch

	H (%)	C (%)	Ash (%)
I	6.57	61.41	—
	6.74	60.99	—
	6.45	60.52	—
	6.41	60.03	—
	6.31	59.99	—
II	6.53	61.28	—
	6.46	60.45	—
	6.46	60.14	0.3
Mean	6.49	60.60	0.3

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(3) The method proposed by Meunier and Gonfard seems rather tedious. *Compt. rend.*, **134** (1932), 1839.

Table 2. (*Concluded*)

"Kuzu" Starch

	H (%)	C (%)	Ash (%)
II	6.37	60.93	—
	6.69	60.76	0.3
	6.31	60.41	0.4
Mean	6.46	60.70	0.4

"Warabi" Starch

	H (%)	C (%)	Ash (%)
II	6.46	60.69	—
	6.69	60.39	—
	6.14	60.57	0.5
Mean	6.43	60.55	0.5

(4) **Melting Points and Specific Rotations.** These are shown in Table 3. In the measurement of optical rotations, ethylene chlorohydrin of b.p. 127.5–128.5° was used as the solvent, the concentration being about 3 per cent. and the temperature about 30° (Table 3).

Table 3.

Origin of starch	Melting point (°C.)	Rotation		
		Conc. (g./dl.)	Temp. (°C.)	$[\alpha]_D$
Potato	170–172	2.986	30.6	+118.3
Corn	170–172	3.025	30.7	+120.1
Sweet potato	169–172	3.013	30.8	+117.1
Wheat	169–171	3.015	31.1	+120.8
"Kuzu"	165–169	3.003	31.2	+118.5
"Warabi"	170–172	3.000	31.1	+118.1

As the light-source for the polarimetric measurement, we used a sodium-flame produced by a glass-work burner: a pinch of asbestos wetted with a strong solution of sodium carbonate or caustic soda and dried in the flame of a Bunsen burner, is fastend with copper wire and put into the flame near the jet of the glass blowing burner. Instead of air blast, a moderate stream of oxygen is supplied from the bomb. The brightness of the light source is comparable with that of a small electric sodium lamp.

Quite recently A. I. Schattenstein(4) reported an analogous idea on the use of oxygen-coal-gas flame as a monochromatic light source of D-line. Sodium chloride and bromide which he used cannot be recommended, for, although the intensity of the flame is great, much smoky sublimate is produced and this makes the air of the laboratory very dirty.

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(4) A. I. Schattenstein, *Z. anal. Chem.*, **98** (1934), 235.