

The Preparation and Properties of Certain Ether Derivatives of Starch†

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Because of its cheapness and commercial availability starch has been employed extensively in the past for uses that require a relatively small change in the starch molecule. It is for these reasons that starch is now being examined for possible transformation into compounds in which a major change in its properties may be effected.

The present work is limited to the preparation and examination of some of the lower alkyl derivatives of starch. It is hoped that the properties of these alkyl derivatives of starch will make them of value in the arts.

Much work has been done on the methyl derivatives of starch for this has been a favorite tool in the hands of those men interested in the molecular structure of starch (1) (2) (3) (4). A few references and patents are available for the ethyl derivative but propyl and butyl derivatives of starch are merely mentioned in the literature (5) (6).

Experimental

Adequate experimental data for the methyl derivatives of starch may be found readily in the literature (1). The original patent of Lilienfeld (6) on the ethyl derivative of starch is satisfactory for use in the preparation of this product.

The propyl derivative of starch is only mentioned in the literature (5). It is, however, readily prepared by our procedure. Its properties are of interest because of its low solubility in water. A procedure developed for obtaining this derivative is:

Thirty grams of corn starch (10-15% moisture), 60 g. of solid sodium hydroxide, 450 g. of a 40% solution of sodium hydroxide, and 277 g. of *n*-propyl chloride are agitated in a stirred, heated autoclave for 24 hours at a temperature of 135-140°C. A grey solid is obtained on steam distillation of the reaction product. This solid is readily purified by dissolving in glacial acetic acid, filtering, and precipitating with water, or by pouring the acetic acid solution into violently agitated water. The white product, which floats to the surface, is filtered, washed with sodium carbonate to remove acetic acid, and then thoroughly washed with distilled water. The yield of the air-dried product is about 30 grams.

No adequate data are available in the literature for the preparation of the butyl derivative of starch. It was prepared in this laboratory by the following procedure.

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Fifteen grams of corn starch, 250 g. of 40% sodium hydroxide, and 160 g. of *n*-butyl chloride are rocked in a heated bomb for 24 hours at 165-170°C. The product is steam distilled to remove butyl chloride, butyl ether, and butyl alcohol. After cooling, a compact, brittle solid is obtained which may be purified by use of glacial acetic acid (cf. propyl derivative). The product is a white, fluffy powder which is not plasticized by acetic acid during the purification process. About 18.4 g. of the alkylated product is obtained. Higher temperatures or higher alkali concentrations must be avoided to prevent the formation of butyl ether which is tenaciously retained by the alkylated product.

Physical Examination

The methyl derivative of starch is water soluble and therefore must meet the competition of cheaper starch products. The ethyl derivative of starch can be made both as water soluble and insoluble derivatives. One alkyl group per glucose residue produces water solubility, whereas two ethyl groups gives a water insoluble product. The latter product is more soluble in organic solvents.

The propyl derivative of starch is definitely water insoluble when two propyl groups per glucose unit have been introduced into the molecule. The butyl derivative of starch is even more like the non-polar type of organic compound. Solubility characteristics can be obtained from Table I in which S indicates soluble, I indicates insoluble, and PS indicates partially soluble.

Table I. Solubility of Alkyl Starches

Solvent	Ethyl Derivative	Propyl Derivative	Butyl Derivative
Acetone	S	S	S
Toluène	S	S	S
Amyl Acetate	S	S	S
Butanol	S	S	S
Petroleum Ether	I	PS	PS
Tetrachloroethane	..	S	S
Ethyl Alcohol (95)	S	S	PS

These alkylated derivatives of starch are compatible with commonly used plasticizers such as dibutyl phthalate, tributyl phosphate, ethox, flexol, tributyl citrate, and hercolyn.

Because of the nature of the compounds no accurate melting point can be obtained for these derivatives. The observable physical change can be described as a shrinking or softening.

Table II. Softening Points of Alkyl Starches

Ethyl Derivative of Starch	140-145°C. (uncorr.)
Propyl Derivative of Starch	105-110°C. “
Butyl Derivative of Starch	73- 76°C. “

As might be expected, the specific gravity of the alkyl ethers of starch vary with the length of the alkyl group introduced. The products have about the same specific gravity as the corresponding alkyl ethers of cellulose and hence have a large spreading power as against the more dense materials such as the acetate or nitrate of starch or cellulose.

Table III. Specific Gravity of Alkyl Starches

Product	Specific Gravity	Temperature
Ethyl Derivative of Starch	1.14	27°C.
Propyl Derivative of Starch	1.05	28°C.
Butyl Derivative of Starch*	.88	28°C.

* Kerosene used as the liquid.

The viscosity of these alkylated products varies inversely as the chain length. The higher alkyl derivatives require more drastic means in their preparation and this is reflected in the degradation which contributes to the low viscosity. Table IV contains the viscosity in centipoises of these derivatives as determined in a 5% toluene solution using an Ostwald viscosimeter.

Table IV. Viscosity of Alkyl Starches

Product	Time in Seconds	Viscosity in Centipoises
Ethyl Derivative of Starch	586	2.92
Propyl Derivative of Starch	390	1.97
Butyl Derivative of Starch	210	1.06

Summary

The lower alkyl derivatives of starch have been prepared and characterized. These derivatives at present are costly to make and hence their use must be justified. As the character of these compounds becomes more widely known and better procedures for their production developed, uses for them will justify the volume of production necessary for commercial practicability.

Bibliography

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