

Derivatives of Starch. 1. Historical Review of the Acetyl Derivatives of Starch¹

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Acetyl derivatives of starch were first prepared by Schutenberger (1, 14, 36, 53, 54) in 1865, at which time he noticed two types of derivatives. One is soluble in water, while the other is insoluble in water but soluble in alcohol and glacial acetic acid. He reported in 1869 that by using acetic anhydride as the acetylation agent and a temperature of 140°C., an acetyl derivative of starch is formed, while at 160°C. a derivative of dextrin is formed (12, 35, 37).

Michael (26) has shown by visual observation that the starch granule is unaltered upon saponification after acetylation with acetic anhydride, while the presence of even small quantities of acetic acid in the acetylation mixture gives some modification. The use of acetyl chloride was shown to give an acetylated dextrin.

The use of sulfuric acid as a catalyst in the acetylation of carbohydrates was first studied by Franchimont (11).

Skraup (38) showed that low temperatures and low sulfuric acid concentration yield more complex products in the acetylation of starch than when high temperatures and high sulfuric acid concentrations are used. He also prepared a chlorinated acetyl derivative of starch by treating starch with acetic anhydride saturated with hydrogen chloride (39).

Syniewski (47) prepared an acetyl derivative by acetylating starch with acetyl chloride and barium carbonate. Pregl (29) acetylated soluble starch with acetic anhydride.

Cross, et al. (8) prepared the lower acetyl derivatives of starch by heating starch in acetic acid at 100°C. Their work indicated that the extent of acetylation is proportional to the time of heating and the ratio of acetic acid to starch.

Law (23) observed that starch did not react with the acetylation medium of Cross, Bevan, and Briggs, which consists of acetic anhydride, zinc chloride and glacial acetic acid.

Traquair (49) obtained acetyl derivatives by heating starch in glacial acetic acid or acetic anhydride at 90°C.

Boeseken, Berg, and Kerstjens (4) studied the catalytic effect of hydrogen chloride, hydrogen bromide, hydrogen iodide, sulfuric acid, zinc chloride, sodium acetate, and pyridine upon the acetylation of starch with acetic anhydride at 35°C.

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The use of amines such as pyridine and quinoline for the preparation of acetyl derivatives of starch has been investigated by Pringsheim and Lassman (30), Bergman and Knehe (3), Friese and Smith (13), Brigl and Schinle (5), Reich (31) and Reich and Damansky (32, 33).

The use of the Twitchell reagent was investigated by Escales and Levy (10) as a possible catalyst in the acetylation of starch and was found to give very rapid acetylation.

Peiser (27) treated dry starch with acetic anhydride in the cold and obtained an acetyl derivative, which when treated in toluene with phosphorus pentachloride at 105°C. yielded a chlorinated acetyl derivative.

Haworth, Hirst, and Webb (15) acetylated starch by use of the Barnett catalyst (2), sulfur dioxide and chlorine. The temperature of the reaction did not seem to affect the nature of the final product.

Tsuzuki (50) acetylated starch by a method which he claims avoids partial depolymerization of the starch. Zinc chloride is used as the catalyst. He also acetylated starch in non-aqueous solutions, using glycerol, zinc chloride, and acetic anhydride (52). The use of sodium or potassium thiocyanates as catalysts was also studied and found to give an acetyl derivative (51).

Clark and Gillespie (7) have studied the preparation of acetyl derivatives of starch using glacial acetic acid at the reflux temperature of the solution with or without sodium acetate as a catalyst. Sodium acetate was found to give a slower reaction rate.

Hughes, Macbeth, and Winzor (17) prepared acetyl derivatives in one day by pre-treating the starch with boiling water and then drying with ethanol. The acetylation is carried out with acetic anhydride and five per cent of sulfuric acid.

Sutra (45) reacted starch with acetic anhydride at 70°C. and obtained maltose octaacetate.

Damansky (9) showed that in an acetylation the sulfuric acid causes degradation of the starch into amylose and biose. Sutra (46) was able to show that both sulfuric and phosphoric acids cause degradation of the starch molecule.

Higginbotham and Richardson (16) showed that with pyridine very little degradation of the starch molecule results while with the Barnett catalyst (2), sulfur dioxide and chlorine, extensive degradation or modification takes place.

Acetyl derivatives can be prepared by treating alkali starch with acetic acid vapors (18), or by a prior treatment with a gas as ammonia, formaldehyde, pyridine or steam followed with acetic acid vapors (19). The use of sulfur dioxide as an acetylation medium or catalyst has been claimed (20, 21, 34). Lorand (24) claims the use of sulfuryl chloride, or magnesium perchlorate as catalysts in the esterification of starch. Starch can be esterified by a pre-treatment with acetic acid and water for one hour at 60° C. followed with glacial acetic acid and acetic anhydride (6). Starch may be acetylated by heating with acetic acid at 80°C. (48).

The use of these derivatives in coating compositions has been claimed. Livering and gelling are prevented by the addition of a small amount of an acid, such as oxalic, phosphoric, tartaric, citric, malic, formic, or acetic (25).

Staudinger et al. (41, 42, 43, 44) and Escales and Levy (10) have determined the viscosities of acetyl derivatives of starch solutions.

Snelling and Boyd (40) proposed the use of a large excess of a concentrated solution of ammonium nitrate having a boiling point greater than 110°C. to produce acetyl derivatives of a lower viscosity.

Darrer and Fiorone (22) calculated the heat of esterification of starch to starch triacetate as 1306.0 K. cal. Their experimental value for this esterification was 1296.5 K. cal. The heat of combustion of starch hexaacetate, $[C_6H_7O_5(OC.CH_3)_3]_2$, is 4499 calories per gram.

Experimental

A series of acetyl derivatives of starch were prepared by refluxing 25 grams of dried starch with a mixture of acetic acid and acetic anhydride. Forty-five ml. of acetic anhydride is slightly more than suffi-

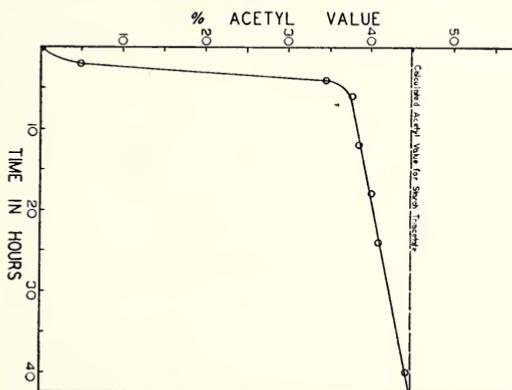


Fig. 1. Acetyl derivatives of starch prepared at reflux temperature. No catalyst.

cient to react with the moisture in the starch and the water of esterification. Two hundred ml. of glacial acetic acid was used. It is apparent that the acetic acid is in excess, so it can act both as a reagent and as a solvent for the ester. The product was recovered by precipitation into water and leached for 24 hours, after which it was filtered, washed and dried. The results appear in Table I and Figure 1. They show that the rate of acetylation is slow until an acetyl value of about four per cent is attained, then very rapid, and finally slow but uniform. The break in the esterification curve is accompanied by a clearing of the viscous solution. It was shown by further experimentation that a large excess of acetic anhydride is unnecessary to prepare these derivatives. Lower reaction temperatures than that used were shown to give acetyl derivatives of a lower acetyl group content.

Table I.—Preparation of Acetyl Derivatives of Starch at Reflux Temperature of Solution.

No.	Time in Hours	Free Acid	Acetyl Value	Yield (in grams)
1.	2	0.13%	4.8%	25.0
2.	4	0.10%	34.5%	33.8
3.	6	0.02%	37.7%	33.2
4.	12	0.01%	38.4%	35.0
5.	18	0.01%	40.0%	38.0
6.	24	0.01%	40.8%	42.5
7.	40	0.06%	44.2%	44.0

Summary

1. The rate of acetylation of starch under reflux with glacial acetic acid and a *minimum* of acetic anhydride is almost linear after an acetyl value of 36% has been obtained. The solutions of starch-acetic acid-acetic anhydride become clear when an acetyl value of approximately 36% is attained. The rate of acetylation between 4 and 35% acetyl value is extremely rapid compared to the other intervals.

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