ACETOLYSIS OF POLYSACCHARIDES II. PREPARATION OF KOJIBIOSE BY THE ACETOLYSIS OF A DEXTRAN PRODUCED BY LEUCONOSTOC MESENTEROIDES NRRL B-1299

ACETOLYSIS OF POLYSACCHARIDES II. PREPARATION OF KOJIBIOSE BY THE ACETOLYSIS OF A DEXTRAN PRODUCED BY *LEUCONOSTOC MESENTEROIDES* NRRL B-1299*

By

Kazuo MATSUDA, Kentarô FUJIMOTO** and Kiyoshi ASO

Department of Agricultural Chemistry, Faculty of Agriculture, Tohoku University, Sendai, Japan

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Preparation of kojibiose by the addition of acetolysis to a dextran of *Leuconostoc mesenteroides* NRRL B-1299 was attempted. By the usual method of carbon : Celite column chromatography, kojibiose and a small amount of nigerose were obtained from the acetolysate of the above dextran.

In the previous paper (1) we have reported that 1, 6-linkage is much less stable to acetolysis than 1, 3-linkage. We have also been able to isolate nigerose from the acetolysate of a dextran produced by *Leuconostoc mesenteroides* NRRL B-421 by carbon : Celite column chromatography.

In 1956, Scott *et al.* (2) pointed out the presence of 1, 2-linkage in some dextrans from the optical rotational shifts due to the formation of a cupro-ammonium complex. According to them, a few of them (e.g. that from *Leuconostoc mesenteroides* NRRL B-1299 or B-1399) contain more than 30 per cent 1, 2-linkage.

It may be presumed that 1, 2-linkage is also fairly resistant to acetolysis, because this linkage is also a linkage attached to a secondary hydroxyl group. We have now attempted to apply acetolysis to the preparation of 1, 2-linked kojibiose and have been able to isolate this sugar in good yield from the acetolysate of the dextran produced by *Leuconostoc mesenteroides* NRRL B-1299 which had been kindly provided by Dr. Senti. According to Scott *et al.* (2), the above dextran seemed to contain only a trace of 1, 3-linkage. However, it has been noticed from our present results that the above dextran contains a small amount of 1, 3-linkage in addition to 1, 2-linkage. It may be expected that this method will be the most favorable one for the preparation of kojibiose, if

* The original report of this work is contributed to Nippon Nogei-kagaku Kaishi (J. Agr. Chem. Soc. Japan).

** Present occupation : A member of the laboratory of "Toyo Brewery Co. Ltd."

the dextran can be obtained in satisfactory yield.

Experimental

(1) *Preparation of the dextran*

Dextran used in this study was prepared by cultivating a strain of *Leuconostoc mesenteroides* NRRL B-1299 nearly in the same manner as reported in the previous paper (1). Yields of the dextran were about 16—25g from 2 *l* of the broth.

(2) *Paper chromatography of the acetolysate*

One gram of the above dextran was acetolyzed by the same method as

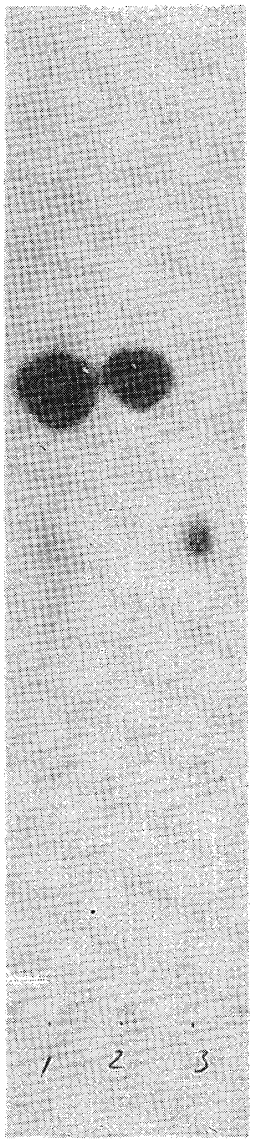

Fig. 1. Paper chromatogram of the acetolysate of the dextran produced by *Leuconostoc mesenteroides* NRRL B-1299.
1. Acetolysate of the dextran
2. Glucose
3. Kojibiose

reported previously (1). As shown in Fig. 1, two spots corresponding to glucose and kojibiose were observed on the chromatogram of the acetolysate and isomaltose was not detected.

(3) *Fractionation of the acetolysate by carbon: Celite chromatography*

Twenty grams of the finely powdered dextran was acetolyzed under the same conditions as described in the previous report (1). Twelve grams of the deacetylated products were obtained.

Twenty two grams of the deacetylated products were fractionated by carbon: Celite column chromatography in the same manner as reported previously (1). The results are shown in Table 1.

Table 1. Fractionation of the acetolysate by carbon: Celite column chromatography.

Fraction*	Solvent used for elution	Paper chromatography	Yield
1	Water	—	—
2— 4	〃	Glucose	10
5— 6	〃	—	—
7	5% Ethanol	—	—
8—10	〃	Kojibiose	7.5
11—15	〃	Nigerose	1.0

* Each fraction was caught in 2 *l*.

Fractions of kojibiose were combined and evaporated to dryness (7.5g) and acetylated by the usual method. 14.1g of crude acetate was obtained. Upon crystallization from ethanol, 9.1 g of crystals was obtained. After repeated fractional crystallizations from ethanol, 1.3 g of α-kojibiose octaacetate and 6.6 g of β-kojibiose octaacetate were obtained. α-Kojibiose octaacetate, m.p. 166°C; β-kojibiose octaacetate, m.p. 117°C. Both acetates showed no depression on admixture with the known specimen.

Fractions of nigerose were evaporated to give 1.0 g of powder, which was acetylated as usual. 1.8 g of the crude acetate was obtained. This was crystallized from ethanol. Recrystallized product showed m.p. 150°C, undepressed on admixture with the known nigerose octaacetate.

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