Heats of Wetting of Polysaccharides. III. Heats of Wetting of Acetylated and Methylated Polysaccharides

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Introduction

The origin of the heat developed when a polysaccharide is thrown into water, is generally ascribed to the interaction between the hydroxyl group of the substance and water molecule. But surprisingly, few experimental facts supporting this opinion have been reported. If this supposition is correct, the heat of wetting of a polysaccharide whose hydroxyl groups are substituted with less hydrophilic groups will become smaller than that of the mother substance.

The author measured the heats of wetting of acetylated starch, glycogen, inulin and konjacmannan, also that of methylated inulin, and obtained smaller values than those of their respective mother substances.

Experimental

Heats of wetting were measured with the apparatus described in the first report of this series(1) under evacuated condition.

The samples of acetylated and methylated polysaccharides were prepared with the following methods.

(1) **Acetylated starch.**—Acetylation was carried out following the method of Kerr and Cleveland(2) who had acetylated limit dextrin. Potato starch, which had been washed thoroughly by methanol with Soxhlet's extractor, was ground to a powder and subjected to acetylation.

(2) **Acetyl glycogen.**— Glycogen purified as

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(1) T. Nakagawa, This Bulletin, **25**, 169 (1952).

(2) R. W. Kerr and F. C. Cleveland, *J. Am. Chem. Soc.*, **71**, 3455 (1949).

described in the first report,⁽¹⁾ was acetylated with a similar method.

(3) **Acetyl inulin.**—Powdered inulin (β form) was treated as reported by W. N. Haworth, E. L. Hirst and E. G. V. Percival.⁽³⁾ The acetylated substance was purified by recrystallization from methanol.

(4) **Acetyl konjacmannan.**—From the preliminary examination, it became clear that β-konjacmannan is not suitable as a starting substance, so the acetylation was performed with α-konjacmannan.

Acetyl determinations were carried out by the method described by W. N. Haworth et al⁽⁴⁾ and the result was as follows:

acetyl starch	43.5 %
acetyl glycogen	—
acetyl inulin	45.0 %
acetyl konjacmannan	44.8 %

(5) **Methyl inulin.**—Methyl inulin was obtained by the simultaneous deacetylation and methylation of acetyl inulin.⁽³⁾

The above-mentioned five samples were subjected to heat measurements after drying in Abderhalden's desiccator under 2/100 mm. Hg at 65°C.

Results and Discussion

The heats of wetting of the above-mentioned substances are arranged in Table 1. in comparison with those of their mother substances.

Table 1

cal./g.

Acetyl starch	5.4	Starch	native	28.2
			pasted	24.6
			retrograded	25.6
Acetyl glycogen	3.1	Glycogen		23.5
Acetylkonjacmannan	6.5	Konjacmannan	α	23.7
			β	16.2
Acetyl inulin	0.3	Inulin	β	23.1
Methyl inulin	1.3		α	17.9
			retrograded	21.2

We see that the acetylated and methylated polysaccharides have much lower values than their mother substances. This fact may give a strong support to the opinion that the heats of wetting of polysaccharides are mainly attributed to the interaction between the hydroxyl groups and water.

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(3) W. N. Haworth, E. L. Hirst and E. G. V. Percival, *J. Chem. Soc.*, 2384 (1932).

(4) W. N. Haworth and H. R. L. Streight, *Helv. chim. Acta.*, **15**, 609 (1932).