COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF CELLULOSE ETHERS OBTAINED BY THE METHYLATION OF CELLULOSE MATERIALS DISPERSED IN QUATERNARY AMMONIUM BASES

Sir:

The methylation of cellulosic materials dispersed in certain quaternary ammonium bases has been reported[1] to proceed as a homogeneous molecular cellulose reaction. The structure of the apparently homogeneous water-soluble methylcellulose prepared in this manner was thought to be similar to the water-soluble methylcellulose obtained by Traube, Piwonka and Funk[2] on methylating a cellulose–copper hydroxide–sodium hydroxide complex. However, since no chemical evidence was presented to substantiate this conclusion, researches on the structure of these partially methylated cellulosic materials have been undertaken in this Laboratory.

The methylation of both wood pulp and ash-free viscose rayon dispersed in 1.8 *N* dimethyldibenzylammonium hydroxide with dimethyl sulfate, according to the procedure of Bock,[1] yields methylated cellulosic materials containing 12 to 16% methoxyl, corresponding to 0.7 to 0.9 methyl group to each $C_6H_{10}O_5$ unit of cellulose. Acetylation of this material with acetic anhydride in pyridine solution, followed by methyl alcoholysis at 125° in the presence of 1% dry hydrogen chloride gave a mixture of partially methylated methylglucosides and α- and β-methylglucosides. The latter crystalline constituents were isolated from the mixture in yields of 30–35%, which after purification was found to be largely α-methylglucoside, m. p. 164–165°; sp. rot. +157.8° (H_2O). The sirupy constituents representing 65–70% of the total alcoholysis mixture, after acetylation with acetic anhydride in pyridine solution, were subjected to distillation under high vacuum. The following fractions were obtained:

Fraction	B. p., 0.1 mm.	% OCH_3	% Yield[a]
I	130–140°	29.5	25–30
II	140–150°	22.5	20–25
III	160–175°	19.5	5–10

[a] Yield based on original weight of acetylated product.

Evidence that Fraction I contained traces of trimethylmonoacetyl methylglucoside (OCH_3, 44.6%) mixed with the predominating dimethyldiacetyl methylglucoside (OCH_3, 30.4%) was shown by the fact that further fractional distillation yielded a fraction (b. p. 130–140°) with a methoxyl content of 31.7%. Fraction II yielded a small amount of crystalline 2-methyltriacetyl α-methylglucoside (OCH_3, 18.5%) with melting point 120–121°, remaining constant when mixed with an authentic specimen.[3] Fraction III yielded crystalline 2-methyltriacetyl α-methylglucoside (m. p. 120–121°), tetraacetyl β-methylglucoside (m. p. 104–105°) and a sirupy product presumably dimethyldiacetyl methylglucoside.

Acetolysis of the methylated wood pulp and viscose rayon (OCH_3, 13.5%) in a manner similar to that described by Lieser[4] gave a 5% yield of cellobiose octaacetate (m. p. 224–225°; sp. rot., +41.5° ($CHCl_3$)).

These experiments confirm the assumption of Bock[1] that the "water-soluble" methylated cellulosic materials obtained by use of the quaternary ammonium bases are very similar in structure to those obtained by Traube, Piwonka and Funk.[2] The results indicate, however, that methylation proceeds by diffusion of dimethyl sulfate into a particle structure, from which it follows that the cellulose component of these materials is not molecularly dispersed in quaternary ammonium bases but rather is dispersed as particles. Slit ultramicroscopic observations[5] of cellulosic materials dispersed in quaternary ammonium bases and of the methylated product dispersed in water verify the above conclusion by showing the presence of microscopic particles approximately 1 μ in diameter.

This work is being extended to other partially methylated cellulosic materials.

Cellulose Department
Chemical Foundation
Boyce Thompson Institute
for Plant Research
Yonkers, New York
Jack Compton

Received October 19, 1938

---

[1] L. H. Bock, *Ind. Eng. Chem.*, **29**, 985 (1937).

[2] W. Traube, R. Piwonka and A. Funk, *Ber.*, **69**, 1483 (1936).

[3] W. N. Haworth, E. L. Hirst and E. G. Teece, *J. Chem. Soc.*, 2858 (1931).

[4] Th. Lieser, *Ann.*, **483**, 132 (1930).

[5] *Cf.* J. Compton, This Journal, **60**, 1807 (1938).