391. *Polysaccharides. Part XXXIV. The Methylation of Cellulose in an Inert Atmosphere.*

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Cellulose has been exhaustively methylated in an atmosphere from which oxygen was excluded. A progressive diminution of particle size of the methylated cellulose as the number of methylations is multiplied has been observed and the result of a chemical assay after fifteen such methylations is recorded. Crystalline tetramethyl glucose was identified as one of the products of hydrolysis and the proportion of this substance found corresponded to a minimum chain length of 700 glucose units for the methylated cellulose. The molecular weight of the cellulose determined osmometrically corresponded to 450 units.

The exhaustive methylation of cellulose in an atmosphere of nitrogen has been undertaken in order to discover (1) if a progressive diminution of the molecular size of the methylated cellulose is to be observed and (2) if an end-group, susceptible of chemical assay, becomes apparent after prolonged methylation in the absence of oxygen (cf. preceding paper).

Cotton sliver was methylated thirty-times in all and a sample was taken for analysis after each methylation. Each treatment with methyl sulphate and 30% sodium hydroxide solution was conducted in the absence of air and all subsidiary operations, such as washing and filtration, were carried out as rapidly as possible and in the cold so long as any alkali was in contact with the cellulose. Methylation of cellulose is a heterogeneous reaction and it is not possible, even with the most extreme care, exactly to reproduce all the conditions of reaction with each methylation. Estimations of methoxyl content, for instance, on the crude product indicate clearly that it is not homogeneously methylated. Furthermore, because of the fibrous character of the crude methylated cellulose, it is not possible to obtain a sample which is uniform in composition. This lack of homogeneity is emphasised when the proportion of a crude methylated product which is soluble in chloroform is considered. It may be taken that a methylated cellulose which contains less than 40% of methoxyl is insoluble in chloroform, so chloroform-solubility is to be regarded as a rough gauge of the degree of methylation. Reference to Table I shows that after even thirty methylations, about 7% of the product was incompletely methylated and insoluble in chloroform. To minimise this difficulty, all the observations on molecular size were made only on that part of each sample which was soluble in chloroform. In any one case, the chloroform-soluble fraction was uniform with respect to methoxyl content.

These facts are to be borne in mind when the results of this investigation, given in Table I, are examined. If the viscosity of a 0·1% solution of the methylated cellulose in chloroform (col. 6) is taken as an index of particle size, it will be seen that there is a progressive diminution of size as the number of methylations to which the cellulose is submitted is increased. Table I shows that eventual complete disruption of the cellulose does not occur. The molecular weight tends towards a minimal value which corresponds to an apparent chain length of about 200 glucose units. This value is reached after 25—30 methylations.

A sample of cellulose (134 g.) which had been methylated fifteen times in nitrogen was now submitted to end-group assay. Two batches (64 g., 70 g.) of methylated cellulose were combined for this purpose. All the methylation treatments which the batches had undergone were as nearly as possible the same, yet the molecular sizes (determined osmometrically) were different (290 and 590 glucose units). The mean particle size of the combined batches was 450 by osmotic pressure measurement and this material yielded an amount of tetramethyl glucose which corresponded roughly to a chain length of 700 glucose units. It is necessary to point out that the proportion of tetramethyl glucose isolated was so small as to bring the figure 700 within the limits of experimental error. It is more accurate to state that tetramethyl glucose was undoubtedly present and the amount of it isolated corresponded to a minimum chain length of 700 glucose units.

In a later summarising publication the results obtained here will be discussed and correlated with those of the preceding paper.

TABLE I.

Methylation of Cotton in Nitrogen.

Batch.	No. of methyl-ations.	% OMe, crude.	% Soluble in $CHCl_3$.	Chloroform-soluble fraction. % OMe.	Chloroform-soluble fraction. $\eta_{sp.}/c$.	Batch.	No. of methyl-ations.	% OMe, crude.	% Soluble in $CHCl_3$.	Chloroform-soluble fraction. % OMe.	Chloroform-soluble fraction. $\eta_{sp.}/c$.
II	1	42·4, 38·1	40·0	42·1	2·33	I—II	7	40·5	67·6	40·7	0·76
III	1	11·2	45·1	41·55	2·81	VII—XI*	8	—	76·4	42·3	0·97
VII	1	40·2	70·4	43·2	1·97	I—II	10	41·9	62·2	45·0	0·68
II	2	40·5	45·5	42·6	1·70	III—IV	10	—	79·1	41·5	0·62
VII	2	—	89·7	43·4	1·725	V—VI	10	—	80·6	43·4	0·61
IX	2	—	66·9	43·2	2·06	VII—XI	10	—	80·7	43·0	0·85
X	2	—	67·0	40·7	1·55	I—VI	15	—	83·1	42·2	0·49†
XI	2	—	74·8	42·6	1·59	VII—XI	15	—	77·9	44·3	0·82‡
II	3	41·8	46·3	41·5	1·30	I—VI	21	—	78·9	44·3	0·24
I—II	4	42·6	47·4	42·6	1·09	I—VI	25	—	74·5	44·2	0·23
I—II	5	38·9	73·3	44·2	1·00	I—VI	30	—	92·8	43·0	0·22

* This notation indicates that five batches (VII to XI) have been combined.

† Mol. wt. (in glucose units) by osmotic pressure, 290.

‡ ,, ,, ,, ,, ,, ,, 590.

EXPERIMENTAL.

Cellulose in the form of raw Egyptian cotton sliver was used in this investigation. The sliver had been mechanically cleaned but had not had any chemical treatment.

The sliver was cut into short lengths (¼" lengths were found to be most suitable) and was methylated in 20 g. batches in a 3 l. stoppered flask provided with mechanical stirring and an arrangement for replacing the air in the flask by nitrogen. The cotton (20 g.) was manually kneaded in 30% sodium hydroxide solution (1 l.) until it was thoroughly wet and all air was expelled. The suspension was placed in the flask and kept for 4—5 hours at room temperature under a slow stream of nitrogen which had been washed with pyrogallol solution. The temperature was then raised to 40—45° and a mixture of methyl sulphate (200 c.c.) and dioxan (200 c.c.) was added at the rate of 2 c.c. per minute. Stirring was continued for ½ hour after this addition and then boiling water (1200 c.c.) was added to the mixture. The dioxan was distilled off on the water-bath for ½ hour. After cooling, the product was collected on a filter consisting of two thicknesses of cloth and was washed free from mineral matter with boiling water (5 l.), followed by cold water (2 l.). After a sample [I (1)] of the product of one methylation had been removed for analysis, the remainder was kneaded with dioxan (200 c.c.) and the treatment with methyl sulphate (200 c.c.) and 30% sodium hydroxide solution (1 l.) was repeated. The alkali solution used throughout was made from caustic soda powder and tap water and the solution was gassed with washed nitrogen before use.

After it had been given three methylations, batch I was combined with batch II, which had been similarly treated, and the combined product [referred to for convenience as I—II (3)] was submitted to further methylation as desired.

Samples for Analysis.—The methylation of cellulose is a heterogeneous reaction and sampling the fibrous product is attended with some difficulty. The accuracy of all analytical figures given must be considered with this difficulty in mind. Samples of about 1 g. were taken after each methylation. The sample was boiled with water (four times), washed with acetone, and dried in a vacuum at 100° for 6 hours. The methoxyl contents of the samples as prepared are given in col. 3 of Table I. Each dried sample was then extracted with chloroform (150—200 parts) by boiling under reflux for 1—2 hours. After this period, the insoluble residue was removed by filtration, and an estimate made of the percentage of soluble material. These values are given in col. 4 of Table I. As filtration was slow, it is clear that these figures represent minimal values.

A comparative estimation of the molecular size of the different samples was arrived at by the determination of the specific viscosity ($\eta_{sp.}$) of solutions of equal concentrations (c = 1·0 g./l.) of the samples in chloroform, an Ostwald pipette at 20° being used. The ratio $\eta_{sp.}/c$ is given in col. 6 of Table I. In two selected examples, the molecular size of the sample has been determined osmotically.

End-group Assay.—An estimate was made of the proportion of end-group present in a methylated cellulose which had been prepared by fifteen treatments with the methylating

agents under nitrogen. Two lots were available for this purpose, namely, the combined batches I—VI (64 g.) and combined batches VII—XI (70 g.). These two lots (each chloroform-soluble) were united and hydrolysed by treatment with glacial acetic acid–8% hydrochloric acid, and the mixture of methylated sugars so produced was converted into the mixed methylhexosides. Details of the procedure have been given in previous papers. The product was fractionally distilled from a Widmer flask at 0·006 mm.; the first two fractions showed the following properties :—

Fraction.	Weight (g.).	$n_D^{19°}$.	% OMe.	$[\alpha]_D^{19°}$.
1	1·065	1·4536	49·85	+16·4°
2	0·915	1·4560	50·3	16·4

It seemed possible from these figures that fraction I contained some methyl lævulate. It was accordingly treated at 80° with barium hydroxide solution for 3½ hours. The product, isolated in the usual way, was distilled at 0·02 mm. :

Fraction.	Weight (g.).	$n_D^{19°}$.	% OMe.
1a	0·088	1·4465	56·3
2a	0·560	1·4550	51·6

The tetramethyl β-methylglucoside produced under these conditions has $n_D^{18°}$ 1·4437, and the trimethyl αβ-methylglucoside, $n_D^{18°}$ 1·4573 (see Hirst and Young, J., 1938, 1249). On this basis, the weight of tetramethyl methylglucoside in fractions 1a and 1b is 160 mg. and this quantity is derived from 134 g. of methylated cellulose. After correction for experimental loss (Averill and Peat, J., 1938, 1244) the yield of tetramethyl methylglucoside corresponds to a chain length of 695 glucose units. The average particle size from the osmotic pressure determinations [see Table I under I—VI (15) and VII—XI (15)], when account is taken of the relative weights of the two batches, is 450 glucose units.

The presence of end-group in this preparation was demonstrated inasmuch as hydrolysis of fraction 1a gave crystalline tetramethyl glucopyranose (30 mg.) which had m. p. 85° and $[\alpha]_D^{18°}$ +80° (equilibrium value in water).

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