390. *Polysaccharides. Part XXXIII. The Methylation of Cellulose in Air and in Nitrogen.*

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An investigation has been made of the methylation of cellulose directly and of methylation of the acetate. Conditions have been varied with respect to (*a*) the number of methylations, (*b*) the temperature of methylation, and, further, a comparison has been made between the products formed when the methylation is conducted entirely in air, entirely in nitrogen, or first in nitrogen and subsequently in air. In every case the purified product was submitted to end-group assay.

The theoretical significance of the results will be discussed in a later paper.

The preparation of methylated cellulose of maximum methoxyl content is readily effected by the method of Haworth, Hirst, and Thomas (J., 1931, 821). In this method, acetone-soluble cellulose acetate (acetyl, 40%) is submitted to simultaneous deacetylation and methylation by treatment, in acetone solution, with methyl sulphate and sodium hydroxide

solution. The fully methylated cellulose so prepared was used by Haworth and Machemer (J., 1932, 2270) in the elaboration of the " end-group " method of assay of the size of polysaccharide chain-molecules.

Fully acetylated cellulose (acetyl, 44·8%) is insoluble in acetone and the acetate described above is prepared by the partial deacetylation, under strictly controlled conditions, of this *triacetate*. The deacetylation is not accompanied by degradation of the cellulose and the acetone-soluble cellulose acetate is in this respect different from the numerous commercial cellulose acetates with which it has been compared (see Hess, *Angew. Chem.*, 1936, **47**, 841).

The preparation and methylation of acetone-soluble cellulose acetate has now been repeated. The closest adherence to the conditions prescribed in the earlier papers has been observed and the conclusions reached previously have been confirmed in all essentials.

The investigation of Haworth and Machemer (*loc. cit.*) has been extended inasmuch as a method has been devised whereby the necessity for the partial deacetylation of cellulose triacetate has been avoided. The method takes advantage of the fact that fully acetylated cellulose, although it is insoluble in acetone, nevertheless swells in dioxan or in a mixture of acetone and dioxan to give a clear, highly viscous solution which is eminently suitable in regard to physical state for the subsequent methylation process. Full details are given under " Cellulose I " in section I of the experimental part.

Sections II and III are concerned with the direct methylation of cellulose, *i.e.*, with the methylation of cellulose (either as cotton sliver or cotton linters) without the intermediate formation of a cellulose acetate. In this method use is made of the fact that alkali brings about extensive swelling of the cellulose fibres with a consequent increased facility of penetration of the methylating reagents. The cellulose is stirred for some hours with a large excess of 30% sodium hydroxide solution until the whole forms a gelatinous mass. Methyl sulphate, dissolved in dioxan, is then added very slowly during 12 hours and the mixture is maintained at the required temperature throughout. The effectiveness of the methylation is to be judged by the fact that after one treatment at room temperature a methylated cellulose having OMe, 41% was obtained.

The conditions of direct methylation were varied in respect to (*a*) temperature of methylation, (*b*) number of treatments with the methylating agents, (*c*) the nature of the surrounding atmosphere, the methylation being conducted in air or in an inert atmosphere of nitrogen. The properties of the methylated cellulose formed under these different conditions are summarised in Table I. In all cases the specimens of methylated cellulose

TABLE I.

The Methylation of Cellulose.

Reference name.	Substance methylated.	Conditions of methylation. Temp.	No. of treatments. In N_2.	No. of treatments. In air.	% OMe in methylated product.	Apparent molecular size (in glucose units). By end-group method.	By osmotic pressure in $CHCl_3$.*	$\eta_{sp.}/c_0$ * in $CHCl_3$.
Cellulose I	Linters acetone-insoluble acetate	55°	—	6	44·5	160	100	0·129
,, II	,, ,,	40	—	6	44·8	180	130	0·178
,, III	,, ,,	55	—	3	44·0	240	190	0·238
,, IV	,, ,,	55	4	—	44·5	240	220	0·269
,, V	Linters acetone-soluble acetate	55	—	2	44·5	170	100	0·155
,, VI	Sliver, direct	15	5	—	43·4	No end group	1540	1·39
,, VII	,, ,,	15, 60	5 †	5	44·6	,, ,,	390	0·490
,, VIII	,, ,,	40, 55	—	8	44·5	150	52	0·060
,, IX	Linters, direct	15	10	—	44·6	No end group	270	0·334
,, X	,, ,,	40, 55	—	6	44·0	170	100—120	0·149
,, XI	,, ,,	40—55	6	—	43·0	No end group	A 1030 B 375	0·687 0·436
,, XII	,, ,,	40—55	3 †	3	44·0	,, ,,	170	0·228
,, XIII	,, ,,	40—55	4 †	16	45·0	240	110	0·157
,, XIV	,, ,,	40—55	—	16	44·3	66	43	0·042

* Details will be published later. † Methylated first in nitrogen and then in air.

were purified by solution in chloroform and precipitation therefrom by the addition of light petroleum. The purified products so obtained were not necessarily homogeneous with respect to molecular size. In fact, it was possible by fractional precipitation in every case to separate the methylated cellulose into parts which showed different specific viscosities in solution. For example, a sample of methylated cellulose III was so separated into fractions which showed $\eta_{sp.}/c$ 0·30 and 0·21 respectively.

With some slight modifications, the technique of Haworth and Machemer for the estimation of end-group in the methylated cellulose was followed. The use of cold concentrated hydrochloric acid as hydrolysing agent was abandoned in favour of a hot mixture of equal volumes of glacial acetic acid and 8% hydrochloric acid. With this reagent the formation of lævulic acid (by the decomposition of the methylated hexoses) was reduced to a minimum. It was nevertheless not possible to eliminate completely this degradative activity of the hydrolysing agent. Careful search was originally made for any acid oxidation products formed during methylation in air. This revealed that even the acetic acid–hydrochloric acid hydrolysing agent was responsible for the formation of a small quantity of lævulic acid (characterised as the ester phenylhydrazone and as the phenylhydrazone-phenylhydrazide). No other acid product was found (see under " Cellulose X ").

The succeeding stages in the analysis were carried out as described by Haworth and Machemer. The mixture of glucosides formed by treatment of the hydrolysed methyl cellulose with alcoholic hydrogen chloride was fractionated by distillation from a Widmer flask and the composition of a fraction was estimated from a consideration of its refractive index and methoxyl content. That a true estimate of the proportion of tetramethyl methylglucoside may be made in this way is shown by the comparative experiments with synthetic mixtures made by Haworth and Machemer (*loc. cit.*) and by Averill and Peat (J., 1938, 1344) and the criticisms and claims of Hess and Neumann (*Ber.*, 1937, **70**, 710, 721) are unfounded.

Experimental.

Section I. The Methylation of Cellulose Acetates.

The source of cellulose in these experiments was technical cotton linters which had copper number 0·08 (by the method of Schwalbe–Braidy; cf. Clibbens and Geake, *J. Text. Inst.*, 1924, **15**, 27T) and iodine number 0·2 (by the method of Bergmann and Machemer, *Ber.*, 1930, **63**, 316, 2304). In this section the term " cellulose " refers to technically bleached cotton linters.

Preparation of Fully Acetylated Cellulose.—To extend the investigation of Haworth and Machemer (*loc. cit.*) conditions were sought for the methylation of the non-reducing but acetone-insoluble cellulose triacetate. This substance was prepared as follows: Cotton linters (50 g.) were soaked in glacial acetic acid (500 c.c.) containing a little chlorine, and the mixture treated in the cold with acetic anhydride (250 c.c.) containing an amount of sulphur dioxide equivalent to that of the chlorine. After standing in the freezing mixture, the material was kept at room temperature until a homogeneous solution was obtained (24 hours). The viscous liquid was diluted with glacial acetic acid (equal vol.) and poured, with efficient stirring, into cold water. The precipitated cellulose acetate was washed free from acid and dried in a vacuum. 400 G. of cotton linters gave 632 g. of the acetate. A sample of the acetate purified by precipitation from a chloroform–acetone–ethyl alcohol solution by means of light petroleum was a white fibrous material which showed copper number 0·05, iodine value 0·2, $[\alpha]_D^{20°}$ − 21° in chloroform (*c*, 2·5), $\eta_{sp.}^{20°}$ 1·2 (0·4% solution in *m*-cresol) (Found: C, 49·8; H, 5·6; CH_3·CO, 44·8. $C_{12}H_{16}O_8$ requires C, 50·0; H, 5·6; CH_3·CO, 44·8%). The molecular weight determined osmometrically (by Dr. W. T. Chambers) corresponded to an apparent chain length of 230 glucose units.

Methylation of Triacetyl Cellulose in Air at 55°.—It was demonstrated in trial experiments that triacetyl cellulose could not be satisfactorily converted into methylated cellulose by the usual process when acetone was used as solvent, since the acetate is neither soluble in acetone nor does it swell in it. When, however, dioxan or a mixture of dioxan and acetone was used as solvent, the acetate swelled to give a clear, highly viscous solution, in which methylation at 55° proceeded with great ease. One treatment with methyl sulphate and aqueous sodium hydroxide solution (30%) yielded a methyl cellulose containing OMe, 41%. The procedure ultimately adopted was the following: Triacetyl cellulose (10 g.), finely powdered, was added, with stirring, to dioxan (200 c.c.) and kept, with occasional stirring, for 12 hours. The highly

viscous mass was diluted with acetone (500 c.c.) to give a clear homogeneous solution. The solution was divided into two equal parts and each portion was treated at 55° with methyl sulphate (250 c.c.) and sodium hydroxide solution (30%, 750 c.c.), the reagents being added in tenth quantities at intervals of 10 minutes. Acetone was added from time to time to compensate for that lost by evaporation. It is essential that vigorous mechanical stirring be maintained throughout the experiment. Boiling water (1500 c.c.) was now added, and the temperature maintained at 95—100° for ½ hour. The product, which separated from the hot water, was filtered off, washed with hot water, and dried in a vacuum. 270 G. of cellulose acetate were treated in this way.

The product of the first methylation was submitted, in batches of 10 g., to further treatment with the methylating agents under identical conditions. Thereafter, batches of 15 g. were used and the material was submitted to six successive methylations in all. The final product was washed with acetone and ether and dried in a vacuum. It was a white powder. Yield, 165 g. (85% of the theoretical). The methylated cellulose was purified by fractional precipitation from solution in a mixture of chloroform (1600 c.c.) and ether (600 c.c.) by the gradual addition of light petroleum (8 l.). Small head and tail fractions (5 g. and 3 g. respectively) were discarded, the bulk of the material (150 g.) separating as a fine white powder. This material decomposed at 225° and showed $[\alpha]_D^{20°}$ — 5·0° (*c*, 3·0 in chloroform) and $\eta_{sp.}^{20°}/c_0$ 0·129 in chloroform. The molecular size by osmotic pressure measurement corresponded to a chain length of 100 glucose units (Found: C, 53·3; H, 8·0; OMe, 44·5. $C_9H_{16}O_5$ requires C, 52·9; H, 7·8; OMe, 45·6%). Further careful fractionation failed to reveal any heterogeneity. This product will be referred to as *methylated cellulose I*.

Determination of the Chain Length, by the End-group Method, of Methylated Cellulose I.—Methylated cellulose I was hydrolysed by heating the purified substance (147 g.) in glacial acetic acid (1500 c.c.) at 90° until solution was complete. Thereafter 10% hydrochloric acid (1500 c.c.) was added, and the solution maintained at 90—95° until polarimetric readings showed the hydrolysis to be complete. The dark coloured solution was filtered with charcoal, the mineral acid neutralised with barium carbonate (470 g.), and the solution evaporated to dryness at 50°. The residue was extracted ten times with chloroform, and the filtered extract (10 l.) evaporated to a syrup under diminished pressure. The product was partially crystalline. Yield, 155 g. (98%).

A preliminary separation of the sugars was achieved by fractional extraction. The product was dissolved in water (1 l.) and extracted fifteen times with chloroform. The extract (1500 c.c.), taken to dryness, gave syrup A_1 (16·5 g.). The aqueous residue was concentrated to 250 c.c. and again extracted with chloroform (300 c.c.). Removal of the solvent from this extract left a syrup which immediately crystallised. From an ethereal solution of this product, crystalline 2 : 3 : 6-trimethyl glucose (12 g.) separated. The ethereal mother-liquors and washings yielded, on evaporation, syrup A_2. The aqueous residue was finally taken to dryness, and crystalline trimethyl glucose (82 g.) separated from the product by recrystallisation from ether. The ethereal mother-liquors and washings, taken to dryness, gave syrup B (24 g.). The total yield of crystalline trimethyl glucose was 94 g. After recrystallisation from ether, this sugar had m. p. 119° and $[\alpha]_D^{18°}$ + 70° (equilibrium value in water; *c*, 2·0).

Fractions A_1, A_2, and B, treated with dry methyl alcohol containing 2% of hydrogen chloride, yielded respectively 16·0, 6·1, and 24·2 g. of glucosides, which were submitted to systematic fractional distillation at 0·01—0·10 mm., a Widmer flask with a vacuum-jacketed column being used. The following fractions were ultimately obtained from fraction A (that is from A_1 and A_2 taken together):

Fraction	1a	2a	3a	4a	5a	6a	7a
Bath temp.	75—90°	95—100°	100—105°	110—120°	115°	125°	110—150°
Weight (g.)	0·180	0·220	0·612	0·832	1·138	3·524	3·846
$n_D^{17°}$	1·4246	1·4499	1·4452	1·4525	1·4560	1·4562	1·4574
OMe, %	24·2	55·6	62·6	54·1	52·0	—	—

From B the following fractions were separated:

Fraction	1b	2b	3b	4b
Bath temp.	70—100°	100—105°	105—120°	120—180°
Weight (g.)	1·27	6·76	11·16	4·28
$n_D^{20°}$	1·4500	1·4556	1·4584	1·4700
OMe, %	45·0	—	—	—

Fraction 1a consisted of a decomposition product; it was optically inactive and was later shown to be methyl lævulate (see under Section II). A little of this substance was present also in fraction 1b.

From the refractive indices and methoxyl contents of the various fractions it is clear that only fractions 2a, 3a, and 4a contain tetramethyl methylglucoside and it is estimated that these fractions contained respectively 0·123, 0·612, and 0·270 g., making a total of 1·0 g. from 147 g. of the methylated cellulose. This yield corresponds to a chain length of 180 units. When the correction for experimental loss (Averill and Peat, *loc. cit.*) is applied, the value becomes 158 units. The identity of the tetramethyl methylglucoside was established by the hydrolysis of part (0·4 g.) of fraction 3a; crystalline 2 : 3 : 4 : 6-tetramethyl glucopyranose (m. p. 87°; $[\alpha]_D^{17°}$ + 82°, equilibrium value in water, *c*, 1·4; OMe, 52·1%) was then separated in 80% yield.

It was further estimated that from 147 g. of methylated cellulose 7·5 g. of dimethyl methylglucoside were produced.

Subsequent determinations of chain length described in this and succeeding sections were carried out in a manner essentially the same as that used in the case of methylated cellulose I. It will be unnecessary, therefore, to give a detailed description of each of the later determinations. The designations A and B for the sugar fractions and a and b for the glucoside fractions will have the same connotation as in the experiment just described.

Methylation of Triacetyl Cellulose in Air at a Lower Temperature.—A further quantity (300 g.) of triacetyl cellulose was simultaneously deacetylated and methylated under the conditions described above except that, after two treatments with the methylating agents at 55°, the subsequent methylations were conducted at 40° and over a longer period (3 hours). Samples of the product were withdrawn after each methylation. These, after purification by precipitation, showed the following properties :

No. of methylations	1	2	3	4	5	6
OMe, %	41·5	43·4	43·8	44·0	44·1	44·4
$[\alpha]_D$ in chloroform	− 3°	—	− 4°	—	—	− 4°
$[\alpha]_D$ in benzene	−13°	—	−16°	—	—	−17°
$\eta_{sp.}^{20°}$ (0·2%) in *m*-cresol	1·28	1·28	1·23	1·12	0·86	0·74
Apparent chain length (from viscosity)	640	640	615	560	430	370

The final product (170 g.; yield, 87%), purified in the manner described, had $[\alpha]_D^{20°}$ − 4·0° (*c*, 5·0 in chloroform) and $\eta_{sp.}^{20°}$ 0·66 (0·2% solution in *m*-cresol) (Found : C, 52·5; H, 8·3; OMe, 44·8%). This material will be referred to as methylated cellulose II.

End-group Assay on Methylated Cellulose II.—The second sample of methylated cellulose (150 g.) was hydrolysed, and the products fractionated, in a manner entirely analogous to that employed in the case of methylated cellulose I. The fractions ultimately separated had the following properties :

Fraction	$1a_1$	$2a_1$	$3a_1$	$4a_1$
Bath temp.	70—80°	100—115°	115—120°	120°
Pressure (mm.)	0·04	0·04	0·04	0·04
Weight (g.)	0·100	0·463	1·066	2·558
n_D (temp.)	1·4230 (17°)	1·4450 (21°)	1·4518 (21°)	1·4550 (21°)
OMe, %	22·6	59·8	51·1	50·6

Fraction	$1a_2$	$2a_2$	$3a_2$	$4a_2$
Bath temp.	80—95°	95—97°	97—100°	100—160°
Pressure (mm.)	0·02	0·02	0·02	0·04
Weight (g.)	0·180	1·615	2·863	3·83
n_D (temp.)	1·4330 (17°)	1·4540 (21°)	1·4550 (21°)	1·4593 (21°)
OMe, %	39·2	52·6	52·3	—

Fraction	1b	2b	3b	4b	5b
Bath temp.	160—165°	165°	115°	120°	120—175°
Pressure (mm.)	30	30	0·02	0·02	0·01
Weight (g.)	0·40	0·58	21·85	10·29	7·93
n_D (temp.)	1·4270 (19°)	1·4545 (19°)	1·4556 (19°)	1·4584 (19°)	1·4690 (19°)

It was evident that tetramethyl methylglucoside was present only in fractions $2a_1$, $3a_1$, $1a_2$, and $2a_2$, which contained respectively 0·392, 0·289, 0·081, and 0·137 g. The total weight of tetramethyl methylglucoside obtained from 150 g. of methylated cellulose was thus 0·90 g., which corresponds, after correction, to a chain length of 176 units. The tetramethyl methylglucoside was characterised by conversion into crystalline 2 : 3 : 4 : 6-tetramethyl glucopyranose.

Methyl lævulate was present in fractions $1a_1$, $1a_2$, and 1b. It was established that this

substance was produced in part at least by the action of the hydrolysing agents on the partially methylated sugars. A mixture of tri- and di-methyl methylglucosides (10 g.) was heated at 90—95° for 7 hours with glacial acetic acid (100 c.c.), concentrated hydrochloric acid (30 c.c.) and water (70 c.c.). After cooling, sufficient barium carbonate (35 g.) to remove the mineral acid was added, and the solvents completely removed under diminished pressure. The residue was exhaustively extracted with chloroform, and the extract evaporated to a syrup. The latter after conversion into the glucosides in the usual way was distilled. The first drop distilling at 160°/30 mm. had $n_D^{15°}$ 1·4280 and clearly was methyl lævulate. The first fraction (0·1 g.) had methoxyl content 46·1%.

The amount of dimethyl methylglucoside produced on hydrolysis of methylated cellulose II (150 g.) was 7·5 g.

Viscosity Measurements in m-*Cresol.*—Viscosity measurements were carried out on solutions of various concentrations of methylated celluloses I and II in *m*-cresol with the following results :

	Methylated Cellulose I.				
c (g./l.)	4·00	0·46	0·23	0·076	
$\eta_{sp.}^{20°}$	0·96	0·075	0·035	0·012	
$\eta_{sp.}^{20°}/c$	0·240	0·163	0·151	0·158	
	Methylated Cellulose II.				
c (g./l.)	2·30	1·00	0·43	0·215	0·073
$\eta_{sp.}^{20°}$	0·76	0·24	0·095	0·043	0·014
$\eta_{sp.}^{20°}/c$	0·330	0·242	0·221	0·201	0·192

The limiting value of $\eta_{sp.}/c$ at zero concentration was utilised in the calculation of chain length from the Staudinger formula and gave values of 150 and 200 units for methyl celluloses I and II respectively. Similar determinations in chloroform solution gave values of 130 and 180, and osmotic pressure measurements of molecular weight values corresponding to 100 and 130 units (Carter, Chambers, and Haworth, to be published).

Methylation of Triacetyl Cellulose in Air under Other Conditions.—In the previous cases described, the cellulose received a minimum of six treatments with the methylating agents. In order that a comparison might be made with the experiments of Haworth and Machemer (*loc. cit.*), fully acetylated cellulose was converted into methylated cellulose by three treatments only with the methylating agents, the conditions being the same as in the preparation of methylated cellulose I. The methyl cellulose prepared in this way (122 g. from 200 g. of the triacetate) was purified by solution in chloroform (1 l.) and precipitation with light petroleum (2 l.) in the presence of anhydrous magnesium sulphate (40 g.). After keeping for 2 days, the solution was decanted and treated with a further volume (4½ l.) of light petroleum. Methylated cellulose III was thus precipitated as a fine, white powder, which after drying in a vacuum at 45° showed OMe, 44·0% and $\eta_{sp.}/c$, 0·275 (c, 0·2 in chloroform).

Methyl cellulose III was not homogeneous, for a small specimen (2·0 g.) was separated from chloroform–light petroleum in two fractions (1·2 g. and 0·4 g.) which showed $\eta_{sp.}/c$ 0·300 and 0·210 respectively (c, 0·2 in chloroform).

The Chain Length of Methylated Cellulose III.—The hydrolysis of methyl cellulose III (100 g.) was carried out by the method described under methyl cellulose I, with one change. To avoid the formation of lævulic acid it was found advisable to alter the concentration of the hydrochloric acid used from 10 to 8%. In the extraction of the methylated sugars the standard procedure was followed and fraction A was converted into the glucosides, which were then distilled at 0·01 mm. Hg as follows :

Fraction	1a	2a	3a	4a
Weight (g.)	0·151	0·514	1·488	1·456
n_D (temp.)	1·4442 (19°)	1·4490 (18°)	1·4561 (18°)	1·4565 (18°)
OMe, %	31·6	57·6	—	—

It was estimated that fractions 1a, 2a, and 3a contained respectively 0·03, 0·34, and 0·05 g. of tetramethyl methylglucoside, the total yield of which was thus 0·42 g. from 100 g. of methylated cellulose III. This yield corresponds, after correction, to a chain length of 240 glucose units.

It is to be observed that the small first fraction contains chiefly methyl lævulate. The formation of this substance has therefore not been avoided completely by the change in concentration of the hydrolysing acid.

Methylation of Triacetyl Cellulose in the Absence of Air.—The methylation was conducted at 55° in dioxan–acetone solution, the usual procedure being followed except that care was

taken to exclude air by the passage of oxygen-free nitrogen through the mixture before and during the methylation. Four methylations in nitrogen gave methylated cellulose IV in 95% yield. The product was purified by solution in chloroform, filtration, and precipitation by the addition of light petroleum. Only the portion soluble in chloroform (85%) was used in the subsequent experiments. The methylated cellulose IV so obtained had OMe, 44·5%. A small portion (0·5 g.) was separated by precipitation from chloroform solution into two fractions (0·45 and 0·05 g.) which showed $\eta_{sp.}/c$ 0·38 and 0·23 respectively (*c*, 0·2 in chloroform).

The Chain Length of Methylated Cellulose IV.—The purified material (100 g.) was hydrolysed as described under methylated cellulose III. The glucoside mixture from fraction A was treated at 70° with barium hydroxide to remove methyl lævulate. Thereafter distillation at 0·01 mm. yielded the following fractions :

Fraction	1a	2a	3a
Bath temp.	110—112°	112—120°	120—125°
Weight (g.)	0·341	0·883	0·892
$n_D^{19°}$	1·4460	1·4538	1·4555
OMe, %	57·7	52·9	51·8

Fractions 1a and 2a contained respectively 0·29 and 0·14 g. of tetramethyl methylglucoside—a total of 0·43 g. This yield, after correction, corresponds to a chain length of 240 glucose units. The tetramethyl methylglucoside was characterised by the hydrolysis of a portion (0·1 g.) of fraction 1a. Crystalline tetramethyl glucose (m. p. 84° alone or in admixture with an authentic specimen) was isolated.

Preparation of Acetone-soluble Cellulose Acetate.—It seemed advisable at this stage to prepare a methylated cellulose by the method of Haworth and Machemer, that is, by the methylation of an incompletely acetylated cellulose which was soluble in acetone. In the preparation of an acetone-soluble acetate from cotton linters the directions of Haworth and Machemer (*loc. cit.* p. 2273) were followed in every detail. It was found necessary, however, to prolong the time of contact with the deacetylating mixture from 24 to 40 hours before precipitation. This retardation was probably due to the laboratory temperature being lower than usual (about 10° during the night). The product obtained, which had the fibrous nature described by Haworth and Machemer, was washed in running water for 3 days, soaked in alcohol, pressed, and dried in vacuum at 50°. A 7% solution of this material in acetone was centrifuged from a small amount of insoluble material, and precipitated by the addition of water. The purified product, after soaking in alcohol and drying in a vacuum, contained $CH_3{\cdot}CO$, 39·6% (equivalent $CH_3{\cdot}CO_2H$ content, 55·2%) and showed $[\alpha]_D^{15°}$ — 15° (*c*, 1·0 in chloroform). The acetate did not reduce Fehling's solution after 2 minutes' boiling but it showed a copper number (Schwalbe–Braidy method) of 1·8. The molecular size of this acetate determined osmometrically was 245 hexose units and $\eta_{sp.}/c_0$ in chloroform was 0·13 (Carter, Chambers, and Haworth, to be published).

Methylation of Acetone-soluble Cellulose Acetate in Air.—The acetate (15 g.), dissolved in acetone (300 c.c.), was methylated at 50—55° by the standard procedure. The product was methylated a second time, the solvent on this occasion being a dioxan–acetone mixture. From 200 g. of the acetate, 133 g. of methylated cellulose V {OMe, 44·3%; $[\alpha]_D^{20°}$ — 19° (*c*, 1·0 in benzene)} were obtained. It was purified in the usual way by precipitation from chloroform solution. The purified product had OMe, 44·5%; $[\alpha]_D^{20°}$ — 8° in chloroform (*c*, 1·0) and $[\alpha]_D^{20°}$ — 20° in benzene (*c*, 1·0). A small portion (1·8 g.) was dissolved in chloroform and separated into two fractions (1·5 g. and 0·2 g.) by the addition of light petroleum. These fractions showed $\eta_{sp.}/c$ 0·21 (*c*, 0·2 in chloroform) and 0·08 (*c*, 0·25 in chloroform) respectively.

The Chain Length of Methylated Cellulose V.—The purified material (100 g.) was hydrolysed by heating with the mixture of glacial acetic acid and 8% hydrochloric acid as described previously. The subsequent extraction, glucoside formation, and removal of lævulic ester were carried out as in the case of methylated cellulose IV. Distillation of the purified glucoside fraction A proceeded as follows :

Fraction	1a	2a	3a	4a
Bath temp.	112°	112—115°	115—120°	120°
Weight (g.)	0·190	0·384	0·882	1·600
$n_D^{21°}$	1·4460	1·4467	1·4528	1·4555
OMe, %	58·1	57·5	54·0	50·4

Fractions 1a, 2a, and 3a contain respectively 0·15, 0·28, and 0·20 g.—a total of 0·63 g. This yield corresponds, after correction, to a chain length of 170 glucose units for methylated cellulose V.

The figures given by Haworth and Machemer correspond, after the correction of Averill and Peat (*loc. cit.*) is applied, to a chain length of 190 glucose units for the methylated cellulose prepared by the former authors.

Section II. The Methylation of Long-staple Cotton.

The source of cellulose was long-staple Egyptian cotton sliver which we obtained by courtesy of Sir Robert Pickard of the Shirley Institute. The sliver was chemically untreated and had been air-dried.

The Cold Methylation of Cotton Sliver in the Absence of Air.—The sliver (15 g.), cut into lengths of ½ inch, was kneaded under 30% sodium hydroxide solution until the air had been expelled from it. A large excess of 30% sodium hydroxide solution (1·5 l.) was then added, and the mixture stirred (gas-tight stirring gland) in a current of nitrogen for 4—5 hours at room temperature. A mixture of methyl sulphate (150 c.c.) and dioxan (150 c.c.) was now added slowly, and the stirring continued for 12 hours. The fibrous product was separated on a copper sieve and washed with cold water, and the excess of water removed by squeezing. The material was then submitted to a repetition of the methylation process under the same conditions. It was found advisable after two such treatments to combine two 15 g. lots and to soak the partially methylated product in dioxan before continuing the methylation. The methylation process was repeated five times (all at room temperature and in nitrogen), and the product washed first with cold water and then with hot. The water was removed by washing with acetone, and the product dried in a vacuum at 60°. The methylated cellulose so obtained retained a fibrous structure. After each methylation, a sample of the product was removed for analysis and purified by solution in boiling chloroform and precipitated by the addition of light petroleum. There was a progressive increase in the solubility of the product in chloroform as methylation proceeded.

Number of methylations	1	2	3	4	5
% Soluble in chloroform	50	65	75	80	85
OMe, % (chloroform-soluble fraction)	†41·7	42·8	43·3	43·3	43·4
*Apparent chain length of chloroform-soluble fraction (in glucose units)	6340	5280	4900	4630	4250

* From the viscosity in 0·1% chloroform solution, using the Staudinger equation.

† The chloroform-insoluble fraction had OMe, 12%.

The methoxyl content was not increased by extending the number of methylations at room temperature beyond five; thus, one sample (15 g.) of sliver was further methylated with the following results:

Methylation	1st	5th	7th	9th	11th	13th	15th
*OMe, %	41·1	43·7	43·5	42·3	42·4	42·1	42·1
*Apparent chain length by viscosity (units)	5000	3400	2700	2200	2800	3200	3200

* Refers to chloroform-soluble fraction.

No useful purpose could therefore be served by continuing the methylation at room temperature beyond five repetitions.

In all, 450 g. of cotton sliver were converted, by five methylations in the manner described, into a methylated product (454 g.) which will be described in this paper as methyl cellulose VI.

Further Methylation of Methyl Cellulose VI at 60° in Air.—The sample of cotton sliver which had received 15 methylation treatments at room temperature in nitrogen was now further treated (in dioxan) with methyl sulphate and 30% sodium hydroxide solution, added simultaneously during 3 hours. The temperature was maintained at 60° and no precautions were taken to exclude air. At the end of each methylation, the reaction was completed and the dioxan removed by raising the temperature to 95—100° for ½ hour. The product was quite insoluble in hot water and was filtered off and washed. The process at 60° was then repeated. There was a progressive fall in the viscosity of the product in chloroform solution, accompanying an increase in the methoxyl content.

Methylation	15th	16th (1st hot)	18th	20th	22nd
*OMe, %	42·1	43·8	44·2	44·5	44·6
†Apparent chain length (glucose units)	3200	2700	1250	800	840

* Of chloroform-soluble fraction.

† From the viscosity of a 0·09% solution in chloroform.

In view of these results, a part (160 g.) of methyl cellulose VI was five times methylated in dioxan solution at 60°. The product (165 g.) was exhaustively extracted with boiling chloroform and, after filtration through a small pad of cotton wool, the chloroform-soluble portion (95%) was precipitated by addition of light petroleum. This product will be referred to as methyl cellulose VII; it had methoxyl content 44·6%, and molecular weight corresponding (by viscosity measurement extrapolated to zero concentration in chloroform) to 490 glucose units and by osmotic pressure measurement to 390 units (Carter, Chambers, and Haworth, to be published).

Purification and Fractionation of Methyl Cellulose VI.—Purification by solution in chloroform and filtration was extremely slow because of the high viscosity of the solution and the gel structure of the insoluble residue. The combined filtrates were concentrated to a thick syrup, which was converted by the addition of light petroleum into a jelly-like mass. The latter was triturated under light petroleum until it hardened to a white solid, which was finally dried in a vacuum at 50° (Found : OMe, 43·4%; $\eta_{sp.}^{20°}$ 1·9 in 0·06% solution in *m*-cresol; yield, 86%).

A part of this material (10 g.) was dissolved in chloroform (1 l.), diluted with alcohol (500 c.c.), and precipitated by the addition of light petroleum (8 l. in all). Three fractions were thus separated and these had $\eta_{sp.}/c$ values in 0·1% solution in chloroform of 3·33, 3·04 and 1·72. No fraction was encountered of shorter chain length.

Hydrolysis of Methyl Cellulose VI.—The purified material (180 g.) was heated at 90° for 4 hours with glacial acetic acid (1800 c.c.). To the semi-solid mass so produced was added 10% hydrochloric acid (1800 c.c.), and the heating continued until the rotation of the solution was constant (8 hours). Subsequent extraction was carried out in the usual way and the glucoside fraction A (16·3 g.) was distilled into a Widmer flask, from which it was then slowly redistilled at 0·01 mm. pressure, as follows :

Fraction	1a	2a	3a	4a	5a
Bath temp.	75—80°	90—120°	120°	120—123°	123°
Weight (g.)	0·291	0·051	0·452	1·281	3·039
$n_D^{15°}$	1·4230	1·4590	1·4568	1·4568	1·4568
OMe, %	23·0	42·0	51·0	—	—

Fractions 3a, 4a, and 5a consist entirely of trimethyl methylglucoside, fraction 2a consists of this glucoside with a little of the substance of fraction 1a. No tetramethyl methylglucoside could be detected. Fraction 1a was shown to be methyl lævulate (Calc. for $C_6H_{10}O_3$: OMe, 23·8%). It was optically inactive and the product of alkaline hydrolysis contained no methoxyl. With sodium nitroprusside in dilute alkali solution, the ester gave an orange colour, changing to pink when acidified with acetic acid. The equivalent (estimated by treatment at 60° for 1 hour with 0·01N-sodium hydroxide) was 134 (Calc. for $C_6H_{10}O_3$: equiv., 130).

Phenylhydrazine in alcohol–acetic acid gave a product which separated from absolute alcohol in colourless needles, m. p. 103°. Lævulic ester phenylhydrazone has m. p. 105—106°.

Hydrolysis of Methyl Cellulose VII.—The hot-methylated cotton (purified by solution in chloroform; 180 g.) was hydrolysed, and the appropriate fraction (fraction A) of the products converted into glucosides by an exact repetition of the process already described in section I (Cellulose III). The glucosides were separated by distillation at 0·01 mm. pressure into the following fractions.

Fraction	1a	2a	3a	4a
Weight (g.)	0·386	0·623	1·076	0·650
$n_D^{15°}$	1·4231	1·4556	1·4562	1·4566
OMe, %	22·9	48·0	50·1	50·0

Fraction 1a was methyl lævulate. Again no tetramethyl methylglucoside is present in detectable amount.

Hot Methylation of Raw Cotton in Air.—For comparison with the similar methylation of linters (see section III) and with the preparation of methylated celluloses VI and VII, long-staple Egyptian cotton was directly methylated in air, three times at 40°, followed by five times at 55°. Apart from the fact that no effort was made to exclude air, the methylation was conducted as described under celluloses VI and VII. The product, methylated cellulose VIII, purified by solution in chloroform and precipitation by the addition of light petroleum, had OMe 44·5%.

The Chain Length of Methylated Cellulose VIII.—The material (94 g.) was hydrolysed by the standard procedure, a mixture of glacial acetic acid and 8% hydrochloric acid being used.

Fraction A of the hydrolysate after conversion into the glucosides was distilled at 0·02—0·03 mm. Hg as follows :

Fraction	1a	2a	3a	4a
Bath temp.	100°	120—123°	123—133°	133°
Weight (g.)	0·010	0·358	0·412	1·702
n_D (temp.)	1·4220 (21°)	1·4450 (17°)	1·4539 (17°)	1·4563
OMe, %	—	61·0	53·0	52·1

Fractions 2a and 3a contained respectively 0·358 and 0·300 g. of tetramethyl methylglucoside. Thus, from 94 g. of methylated cellulose VIII there was obtained 0·66 g. of tetramethyl methylglucoside, a yield which, after correction, corresponds to a chain length of 152 glucose units.

Section III. The Direct Methylation of Cotton Linters.

The cellulose used in these experiments was cotton linters identical with that employed in the work described in section I. Again, the term " cellulose " used here will refer to this commercial cotton linters.

The Cold Methylation of Cellulose in the Absence of Air.—Cotton linters (15 g.) was stirred with 30% sodium hydroxide solution (1500 c.c.) for 4 hours in an atmosphere of nitrogen and thereafter a solution of methyl sulphate (150 c.c.) in dioxan (150 c.c.) was slowly added. The mixture was stirred continuously for 12 hours, a slow stream of nitrogen being bubbled through the solution. The whole process was conducted at room temperature. The insoluble fibrous product was filtered off through a copper sieve, washed with water, and squeezed dry by hand pressure. It was prepared for a second treatment with the methylating agents by soaking it in dioxan and kneading under sodium hydroxide solution. Subsequent methylations were conducted in exactly the same manner as the first. After five such treatments, the fibrous product was filtered off and well washed with cold water, soaked in hot dilute sodium hydroxide solution (to remove methyl sulphate), washed again with hot water and acetone, and finally dried in a vacuum at 50°. 240 G. of cotton linters, methylated in the cold in this manner, yielded 180 g. of methylated cellulose. The course of the methylation was followed by removing samples after each treatment for methoxyl estimation :

No. of methylations	1	2	3	4	5
OMe, %	3·0	5·8	21·8	37·0	41·4

The product after five methylations was only partly soluble in boiling chloroform. The soluble portion (60 g.) had OMe, 44·3% and specific viscosity corresponding to a chain length of 375 glucose units. The insoluble portion, which was in gel form, was separated by filtration through cotton wool, freed from chloroform at 60° under diminished pressure, and submitted to five further treatments with the methylating agents in the cold and in the absence of air. In this way, 105 g. of chloroform-soluble methylated cellulose were obtained from 240 g. of cotton linters. This material (methyl cellulose IX) showed OMe, 44·6% and $\eta_{sp.}^{20°}$ 1·2 (0·2% solution in *m*-cresol).

Hydrolysis of the Chloroform-soluble Methylated Cellulose IX.—The material (100 g.) was shaken with glacial acetic acid (1 l.), kept overnight, and then mixed with 8% hydrochloric acid (1 l.). The mixture was maintained at 90—95° for 7 hours; the mineral acid was then neutralised with barium carbonate (250 g.), the solution taken to dryness, and the residue extracted ten times with chloroform. The extract (10 l.) was concentrated to dryness. Yield of sugars, 105 g. This product was dissolved in water (700 c.c.) and extracted fifteen times with chloroform. The chloroform extract (1000 c.c.), called A_1 in conformity with the usage in the previous sections, was taken to dryness, and the extracted sugars converted into the glucosides by boiling with a 2% solution of hydrogen chloride in methyl alcohol. It was obvious from the previous work that the tetramethyl glucose, if any, would be present in this fraction. The glucosides (9·7 g.), isolated in the usual way, were fractionally distilled at 0·02 mm. pressure, giving the following fractions :

Fraction.	Bath temp.	Weight (g.).	$n_D^{24°}$.	OMe, %.
1a	115°	0·155	1·4545	50·4
2a	115	0·428	1·4550	51·6

Fraction 2a was pure trimethyl methylglucoside and fraction 1a consisted of this glucoside

containing a little methyl lævulate. Tetramethyl methylglucoside ($n_D^{20°}$ 1·4430; OMe, 62·0%) was definitely absent from both fractions.

The Hot Methylation of Cotton Linters in the Presence of Air.—Cellulose (15 g.) was stirred into 30% sodium hydroxide solution (1 l.) and allowed to stand overnight. Dioxan (200 c.c.) was then added, and the mixture treated at 40° with methyl sulphate (200 c.c.) in tenth quantities at 20-minute intervals. After the last addition, stirring was continued at 40° for 1 hour; thereafter boiling water was added, and the temperature maintained at 95—100° for ½ hour. The insoluble product was filtered off and washed with hot water. This product was subjected to further methylation by the addition of dioxan (300 c.c.), followed by 30% sodium hydroxide solution (800 c.c.), keeping overnight, and, after the addition of acetone (300 c.c.), treatment of the emulsion so formed with methyl sulphate at 40° in the manner described above. The cellulose was submitted to four such treatments at 40°, and the product to two further methylations at 55°. The final product was washed with hot water and acetone and dried in a vacuum at 70°. From 360 g. of cotton linters there were obtained 374 g. of methylated cellulose which was almost completely soluble in chloroform. Methylation occurred more rapidly than in the cold process, the methoxyl content after 1, 2, 3, and 4 treatments being 14·0, 36·1, 41·4, and 42·5% respectively (estimated on the chloroform-soluble portion in all cases except the first). There was a progressive fall during methylation in the viscosity values in chloroform.

The methylated cellulose (180 g.) was tested for homogeneity by solution in chloroform and fractional precipitation by the addition of light petroleum. The following fractions were separated :

Fraction	1	2	3	4
Weight (g.)	30	19	127	0·2
$\eta_{sp.}/c$	—	0·150	0·140	0·030
OMe, %	—	—	44·0	—

Hydrolysis of the Methylated Cellulose X.—Fractions 2 and 3 together (140 g.) were dissolved in glacial acetic acid (1400 c.c.), mixed with 8% hydrochloric acid (1400 c.c.), and maintained at 95° for 9 hours. The hydrolysis products were extracted and converted into the glucosides by a process identical with that described under cellulose IX. Systematic fractional distillation at 0·01 mm. pressure yielded the following products :

Fraction	$1a_1$	$2a_1$	$3a_1$	$1b_2$	$2a_2$
Bath temp.	110—115°	115—125°	125°	115—130°	130°
Weight (g.)	0·414	1·598	5·290	0·645	1·380
$n_D^{17°}$	1·4462	1·4555	1·4570	1·4532	1·4570
OMe, %	60·1	52·6	51·0	55·0	51·1

From these figures it was estimated that fractions $1a_1$, $2a_1$, and $1a_2$ contained respectively 0·414 g., 0·222 g., and 0·230 g. of tetramethyl methylglucoside. Methyl lævulate was absent from all fractions.

The yield of tetramethyl methylglucoside from 140 g. of methylated cellulose was thus 0·87 g., which, corrected for experimental loss, corresponds to a chain length of 171 units.

The Hot Methylation of Cotton Linters in the Absence of Air. Methylated Cellulose XI.—Sodium hydroxide solution was freed from oxygen by bubbling through it oxygen-free nitrogen for 1 hour before use. Dioxan was purified by leaving this solvent in contact with solid ferrous sulphate for several days.

Cotton linters (15 g.) was soaked in water to remove air bubbles, squeezed out, and soaked in 30% sodium hydroxide solution for 12 hours. Dioxan (200 c.c.) was then added, the temperature raised to 40°, and methyl sulphate (200 c.c.) added slowly during 3 hours. During the process of soaking and methylation a continual stream of nitrogen (washed in alkaline pyrogallol) was passed through the mixture. Hot water (1½ l.) was now added, the temperature raised to 95—100° for ½ hour, and the methylated product then filtered off and washed with warm water. The cellulose was treated six times in all with the methylating agents, the first three methylations being conducted at 40°, the final three at 55°. After the second methylation, acetone was added in addition to dioxan. Yield, 133 g. from 120 g. of cotton linters. The methylated cellulose (dried at 45° in a vacuum) had OMe, 41·2% and was incompletely soluble in chloroform. Purification was effected by extraction with boiling chloroform (4 l. to 30 g.). The extract, filtered through cloth and concentrated, was precipitated by the addition of light petroleum. Yield, 75 g. of chloroform-soluble methyl cellulose XI (Found : OMe, 43·0%).

A portion (4 g.) was fractionated by solution in chloroform and precipitation with light petroleum as follows :

Fraction.	Weight (g.).	$\eta_{sp.}^{20°}$.*
A	2·4	0·99
B	1·2	0·54

* 0·1% solution in chloroform.

Obviously the material is not physically homogeneous.

Hydrolysis of the Methylated Cellulose XI.—The hydrolysis with glacial acetic acid and 8% hydrochloric acid, the isolation of the methylated sugar, and the conversion into the glucosides were carried out under the same conditions as obtained in the previous experiments. The lower-boiling glucoside fraction A (which would contain any tetramethyl methylglucoside formed) was fractionally distilled at 0·03 mm. as follows :

Fraction	1a	2a	3a
Bath temp.	125°	125—127°	127°
Weight (g.)	0·208	0·660	0·930
$n_D^{20°}$	1·4535	1·4555	1·4555
OMe, %	51·4 51·8	51·6	—

Fractions 2a and 3a consist of pure trimethyl methylglucoside; fraction 1a may contain besides a little methyl lævulate and tetramethyl methylglucoside. Consideration of the refractive index of this fraction in conjunction with its methoxyl content indicates that, if tetramethyl methylglucoside is present at all, its amount cannot exceed 20—30 mg. This amount obtained from 70 g. of methylated cellulose corresponds to a chain length for the latter of over 2000 glucose units.

Methylated Cellulose XII.—It has been shown that raw cotton, on methylation and hydrolysis, yields no end-group if the preliminary stages of methylation are conducted in the cold and with the exclusion of air (see methylated celluloses VI and VII). The effect of preliminary methylation in the absence of air at a higher temperature was now investigated, linters being used as the source of cellulose.

Cotton linters (120 g.) in batches of 20 g. was methylated three times at 40° under the standard conditions for methylation in the absence of air. The product was mixed, redivided into six portions, and each portion submitted to three further methylation treatments at 55° in the presence of air. The solvent in each case was a mixture of acetone and dioxan. The product of six methylations (155 g.) was dissolved in chloroform (1500 c.c.) and treated with light petroleum (5 l.). The precipitate (48 g.) was removed in the centrifuge, and the supernatant liquor mixed with light petroleum (4 l.). A second fraction (103 g.) of methylated cellulose XII was thus obtained which showed OMe, 44·0% and $\eta_{sp.}/c$ 0·25 (*c*, 0·15 in chloroform). A small portion (0·5 g.) of the latter was separated into two fractions (0·3 and 0·15 g.) by precipitation from chloroform solution. These fractions showed $\eta_{sp.}/c$ 0·28 and 0·22 respectively.

The Chain Length of Methylated Cellulose XII.—The material (98 g.) was hydrolysed with a mixture of glacial acetic acid and 8% hydrochloric acid, and the products extracted by the usual procedure. Distillation of the glucosides of fraction A at 0·04 mm. proceeded as follows :

Fraction	1a	2a	3a	4a
Bath temp.	110—130°	130—135°	135°	135°
Weight (g.)	0·090	0·252	0·427	0·820
$n_D^{15°}$	1·4445	1·4558	1·4568	1·4570
OMe, %	33·5	51·0	51·5	51·5

Tetramethyl methylglucoside is apparently absent from all fractions. However, since the methyl lævulate (responsible for the low methoxyl content of fraction 1a) may have masked the presence of a small amount of tetramethyl methylglucoside, it was considered advisable to remove the former. Accordingly, fractions 1a—4a were combined, dissolved in water, and warmed at 65° with a saturated solution of barium hydroxide (5 c.c.) for 1 hour. Thereafter, the solution was neutralised with carbon dioxide and evaporated to dryness and the glucosides were extracted from the residue with chloroform–ether. Redistillation of the glucosides from a Widmer flask at 0·02 mm. gave the following fractions :

Fraction.	Bath temp.	Weight (g.).	$n_D^{20°}$.	OMe, %.
1	120°	0·150	1·4530	52·8
2	120—125	0·424	1·4550	51·5

It is evident from these figures that fraction 1 contains a trace of tetramethyl methylglucoside. This is computed to be 0·03 g., an amount within the experimental error of the method. Without correction, this yield corresponds to a chain length of 4000.

Methylated Cellulose XIII.—The inference from the experiment just described is that the normal methylation of an end group in cellulose which takes place in the presence of air may not occur if the preliminary methylation is carried out in a nitrogen atmosphere. To investigate this point further, cotton linters (40 g.) was methylated three times at 40° and once at 55° in an atmosphere of nitrogen. The product was divided into two portions (A) and (B), each of which was submitted to further methylation at 50—55° in the presence of air. In the case of (A) the whole of the appropriate amount of 30% sodium hydroxide solution was added at the beginning of each methylation, whereas in the case of (B), the alkali and the methyl sulphate were added simultaneously in ten aliquot parts. The effect of this difference in conditions of methylation on the molecular size of the product is shown in the following table :

No. of methylations in air	7	10	15
Sample (A), $\eta_{sp.}/c$	0·300	0·250	0·145
,, (B) ,, ...	—	0·330	0·245

The method of methylation to which (A) had been submitted was now utilised for the conversion of linters (120 g.) into methylated cellulose XIII, which was obtained after four methylations in a nitrogen atmosphere, followed by sixteen methylations in air. The product (125 g.), after purification by precipitation from a filtered chloroform solution by the addition of light petroleum, had OMe, 45·0%; $\eta_{sp.}/c$ 0·175 (*c*, 0·2 in chloroform) and $[\alpha]_D^{20°}$ — 18° (*c*,1·0 in benzene). A small sample was separated into two fractions (0·3 and 0·14 g.), which showed $\eta_{sp.}/c$ 0·21 and 0·14 (*c*, 0·24 in chloroform) respectively.

Chain Length of Methylated Cellulose XIII.—The material (60 g.) was hydrolysed, and the products extracted, under the standard conditions. The two extracts A_1 and A_2 were separately converted into the glucosides, and the latter freed from methyl lævulate by treatment with barium hydroxide solution (see under methylated cellulose IV). Fraction A_1 was distilled at 0·01 mm. as follows :

Fraction.	Bath temp.	Weight (g.).	$n_D^{19°}$.	OMe, %.
1a	115°	0·156	1·4470	58·0
2a	116	0·650	1·4541	53·1
At this point fraction A_2 was added, and the distillation continued.				
3a	116—118	0·525	1·4554	52·7
4a	118—125	0·970	1·4560	52·3

Fractions 1a, 2a, and 3a contain respectively 0·12, 0·11, and 0·03 g. of tetramethyl methylglucoside, the total yield of which (0·26 g.) corresponds, after correction, to a chain length of 240 glucose units.

Prolonged Methylation of Linters in Air. Methylated Cellulose XIV.—A portion of methylated cellulose X (which had been prepared by the methylation of linters six times in air) was now submitted to ten further treatments with the methylating agents at 55° under the conditions specified for methylation in air. Methylated cellulose XIV is thus the product of sixteen methylations of cotton linters in air. It was fractionated by precipitation from a chloroform solution; the main fraction (61 g.) had OMe, 44·3%. A small portion (0·5 g.) of the latter was further separated into three fractions (0·35, 0·10, 0·05 g.) by the same method. These fractions showed $\eta_{sp.}/c$ 0·51 (*c*, 0·5), 0·32 (*c*, 0·74), and 0·27 (*c*, 0·6) respectively in chloroform solution.

Chain Length of Methylated Cellulose XIV.—Application of the standard procedure to the purified material (56 g.) gave the glucoside fraction A (7·2 g.), which after purification by treatment with barium hydroxide solution was distilled at 0·01 mm. as follows :

Fraction	1a	2a	3a	4a
Bath temp.	120°	120—125°	125—140°	140°
Weight (g.)	0·286	0·257	1·162	0·656
$n_D^{17°}$	1·4442	1·4460	1·4522	1·4572
OMe, %	60·2	57·2	53·4	51·4

Fractions 1a, 2a, and 3a contain respectively 0·286, 0·221, and 0·447 g. of tetramethyl methylglucoside, the total yield of which (0·954 g.) corresponds, after correction, to a chain length of 66 glucose units.

A Search for Oxidation Products.—The whole of the hydrolytic products of methylated cellulose X were submitted to a careful investigation with the view to the separation of any acid products that might have been formed.

The hydrolysis products remaining in aqueous solution after the extraction of the tetramethyl glucose-containing fraction by means of chloroform extract A consisted chiefly of tri- and di-methyl glucoses and was partially crystalline. From this material (120 g.) 2 : 3 : 6-trimethyl glucose was separated in crystalline form from a methyl alcohol–ether mixture. The syrup (60 g.) obtained on evaporation of the mother-liquors was dissolved in a little water and made alkaline by the addition of baryta, the excess of which was then removed by passing carbon dioxide. The solution, after filtration, was evaporated to dryness, and the residue extracted with chloroform (50 c.c.) and ether (300 c.c.) to remove the methylated sugars. The brown residue of barium salts was extracted twice with boiling ether and dissolved in water. A slight deficiency of N-sulphuric acid (4·5 c.c.) was added, the barium sulphate removed on the centrifuge, and the clear solution evaporated to dryness (a little acetic acid distilled with the water). The residual syrup was extracted with boiling ether (five times), the filtered extracts yielding, on evaporation, a reducing syrup (0·2 g.) which was acid in reaction. This material was distilled at (bath temp.) 100—115°/0·02 mm. The residue in the flask (0·1 g.) was reducing and non-acidic. The distillate ($n_D^{17°}$ 1·4420), which crystallised completely, was lævulic acid. It had m. p. 32°, was optically inactive and contained no methoxyl. Titration with standard alkali shows its equivalent to be 111 (calc., 116). Phenylhydrazine in acetic acid gave with the distillate a colourless phenylhydrazone, m. p. 109° (Found : N, 13·9. Calc. for $C_{11}H_{14}O_2N_2$: N, 13·6%).

The barium salts residue was now examined. This was obtained originally when the acid hydrolysing agents (acetic and hydrochloric acids) were partly neutralised by barium carbonate and hence would consist chiefly of barium chloride and barium acetate. The residue, dissolved in water, was treated with excess of dilute sulphuric acid and, after filtration, the excess of the sulphuric acid and most of the hydrochloric acid were removed by the addition of lead carbonate. The solution was filtered, concentrated, and cooled to 0°, and lead chloride separated. Hydrogen sulphide was passed through the solution, the lead sulphide filtered off, and the solution aerated until free from hydrogen sulphide and treated with a slight excess of silver carbonate to remove the remaining chloride. It was necessary finally to remove colloidal silver by passing hydrogen sulphide in the presence of charcoal. The clear colourless filtrate was aerated and evaporated to dryness in a vacuum. The residue was a colourless glass (2 g.), which was acid to litmus and was optically active ($[\alpha]_D^{20°}$ + 15° in mineral acid). It was reducing and had a large ash content in which were indications of sodium, calcium, and aluminium (probably derived from the lead carbonate). Further purification was effected by solution in dilute sulphuric acid and exhaustive extraction with chloroform. The extract yielded 50 mg. of a viscid syrup. The mineral acid was removed from the aqueous solution by the addition of baryta, the filtered solution taken to dryness, and the residue extracted with chloroform. In this way 0·55 g. of a viscous acid syrup was obtained and was added to the previous extract. The syrup, which was reducing, was exactly neutralised with baryta in aqueous solution. The neutral solution was evaporated to dryness, and the residue extracted five times with boiling ether. The final residue, dissolved in water, was treated with a slight deficiency of 0·1N-sulphuric acid, the acid solution taken to dryness, and the product extracted with boiling chloroform. The residue (0·2 g.) was a hard glass and had no acidic properties. The chloroform extract was a syrup (0·3 g.), which after distillation at 0·02 mm. pressure showed $n_D^{16°}$ 1·4410 and crystallised completely. It contained no methoxyl and appeared to be chiefly lævulic acid (Found : equiv., 125. Calc. : equiv., 116). Treatment of this acid with phenylhydrazine (2 mols.) at 100° yielded the phenylhydrazide of lævulic acid phenylhydrazone, m. p. 181° (Found : C, 68·7; H, 6·8; N, 18·9. Calc. for $C_{17}H_{20}ON_4$: C, 68·9; H, 6·8; N, 18·9%).

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