318. *Addition Compounds of the Carbohydrates. Part IV. Potassium Hydroxide Compounds of the Methylglucosides, Maltose, Amylose, and Cellulose.*

By W. J. Heddle and E. G. V. Percival.

It is shown that addition *compounds* of the type $C_7H_{14}O_6$,KOH can be prepared from α- and β-methylglucosides, and since 6-methyl glucosazone can be isolated after methylation of these compounds, it is concluded that the $\cdot CH_2\cdot OH$ group is involved in complex formation. The *compound* $C_{12}H_{22}O_{11}$,3KOH, derived from maltose, has been studied, and after methylation a partly methylated methylmaltoside was obtained from which 2-methyl glucose and 2 : 6-dimethyl glucose derivatives have been isolated, indicating the position of the original potassium hydroxide residues to be at the reducing group and probably at positions 2 and 6 in the non-reducing glucopyranose unit.

Amylose has been shown to give rise to an addition *compound* of the type $(C_6H_{10}O_5,KOH)_x$, and methylation gave a partly methylated amylose yielding 2-methyl glucose derivatives on hydrolysis. A similar result was obtained for the corresponding cellulose *derivative* and in neither case were derivatives of the expected 6-methyl glucose isolated. It is suggested that the $\cdot CH_2\cdot OH$ residues of cellulose are not available for complex formation, being involved in cross linkages.

In an attempt to throw some light on the constitution of the alkali hydroxide complexes of the polysaccharides, the work reported in Parts I, II, and III (J., 1934, 1160; 1935, 648; 1936, 1765) has been extended. Although it was previously thought that methylglucosides did not form addition compounds with potassium hydroxide, yet from both α- and β-methylglucoside equimolar *compounds* with the base have been obtained by precipitation with ether. These were methylated under the conditions previously employed, and after suitable treatment 6-methyl glucosazone was isolated, which is taken as evidence of the participation of the primary hydroxyl residues in complex formation. The yields of monomethyl methylglucoside so obtained were low (5%), indicating the instability of the complex (cf. the yield of 20% of methylglucosides obtained by methylating potassium hydroxide–glucose under the same conditions). The alkali-combining power of the $\cdot CH_2\cdot OH$ residue is therefore low but definite, in accordance with Hirsch and Schlags's view, based on physical measurements (*Z. physikal. Chem.*, 1929, *A*, **141**, 387), that glucose can behave as a weak dibasic acid. It has been shown previously that in the potassium hydroxide complexes of sucrose and cellobiose primary alcoholic residues are involved in complex formation.

Titration experiments (Part I, *loc. cit.*) indicated that maltose could combine with a maximum of three potassium hydroxide molecules as in the case of lactose but in contrast to cellobiose, which only takes up two. Maltose was the most acidic sugar examined by Hirsch and Schlags (*loc. cit.*), who recorded $K_1^{25^\circ} = 11{\cdot}6\times10^{-13}$ and $K_2^{25^\circ} = 7{\cdot}7\times10^{-14}$. Controlled methylation of the tribasic maltose *complex*, now isolated, gave rise to a mixture of partly methylated methylmaltosides in 10% yield, from which by hydrolysis, followed by acetylation and high-vacuum distillation, di- and mono-methyl glucose acetates were separated. 6-Methyl glucosazone was isolated from the dimethyl fraction, and the amide

derived from the dimethyl γ-gluconolactone obtained on oxidation failed to give the Weerman test. These facts, coupled with the failure to isolate any dimethyl osazones, show that the substance was 2 : 6-dimethyl glucose triacetate.

The monomethyl glucose proved to be 2-methyl glucose, for osazone formation yielded exclusively glucosazone, and the amide prepared from the γ-lactone obtained on oxidation again failed to give the Weerman reaction. In the alkali complex, therefore, potassium hydroxide residues are associated with the reducing group (since methylmaltosides were obtained) and with positions 2 and 6 in one of the glucopyranose fragments. By analogy with lactose it is suggested that the non-reducing glucose fragment is involved in this " secondary substitution," since in Part III (*loc. cit.*) it was shown that two out of the three potassium hydroxide residues in the lactose complex were concerned with the galactose fragment. Furthermore, since no 6-methyl glucose could be detected in the monomethyl glucose fragment, it would appear that the attachment to position 2 is stronger than to position 6 in this case, which is remarkable, since α- and β-methyl-glucosides, sucrose, and cellobiose have the $\cdot CH_2 \cdot OH$ group of glucose involved in complex formation. The greater reactivity of the hydroxyl group on C_2 than of that on C_6 applies also to cellulose and amylose, and it is to be noted that in the tripotassium hydroxide derivative of lactose (Part III, *loc. cit.*) position 2 is also concerned.

Karrer (*Helv. Chim. Acta*, 1921, **4**, 169) has recorded the isolation of a number of amylose–alkali complexes of the formula $(C_6H_{10}O_5)_2$,NaOH from aqueous solvents. We now find that treatment of amylose acetate with an excess of alcoholic potassium hydroxide yields a *product* approximating in composition to $(C_6H_{10}O_5,KOH)_x$. Some degradation took place on methylation, but a partly methylated amylose acetate was isolated from which, on hydrolysis and fractionation, a monomethyl glucose tetra-acetate was obtained; this appeared to be identical with that isolated from maltose, for it gave rise exclusively to glucosazone. A similar product was obtained from the degraded portion, so the methylation appears to have been restricted to C_2. It is considered likely that the partly methylated amylose acetate is not a mixture of amylose acetate and 2-methyl amylose triacetate, but amylose acetate which is substituted by methyl groups on about one in every six glucopyranose units. It is certain that, even if all the gluco-pyranose units of amylose carry one potassium hydroxide residue, and this would appear possible from the titration, a large proportion will escape substitution by methoxyl on account of the unstable nature of the linkage, just as potassium hydroxide–glucose fails to give a quantitative yield of methylglucoside under similar conditions. The evidence presented is thus in harmony with the view that the potassium hydroxide is associated with the hydroxyl group on C_2 in the α-glucopyranose units of amylose.

The composition of alkali cellulose has been the subject of controversy for many years, but although the formulation $(C_6H_{10}O_5)_2$,NaOH has been strongly supported for the sodium hydroxide compound (Vieweg, *Ber.*, 1907, **40**, 3876; Rassow and Wolf, *ibid.*, 1929, **62**, 2949), other workers (Gladstone, J., 1852, **5**, 17; Percival, Cuthbertson, and Hibbert, *J. Amer. Chem. Soc.*, 1930, **52**, 3257) have favoured the structure $(C_6H_{10}O_5,NaOH)_x$. The corresponding *potassium hydroxide–cellulose* was prepared according to the method described by the last authors for the sodium analogue, and found to correspond closely to the 1 : 1 formula. Methylation with anhydrous methyl sulphate yielded a fibrous, partly methylated product of variable methoxyl content (OMe, 5—9%), from which by hydrolysis, removal of glucose by fermentation, acetylation, and distillation, 2-methyl glucose tetra-acetate was isolated. In this case, as in the others dealt with in this paper, the free sugar gave rise exclusively to glucosazone, but it was unfortunate that 2-methyl glucose phenylhydrazone could not be crystallised. This was doubtless due to the presence of impurity, since it was shown by Munro (Thesis, Edinburgh, 1936) that this substance was exceedingly difficult to prepare from impure 2-methyl glucose. Careful search, however, failed to reveal the presence of any other methylated glucose, and the inference is therefore drawn that in cellulose position 2 in the β-glucopyranose unit is the significant factor in linking the alkali hydroxide to the polysaccharide. Lieser and his co-workers (*Annalen*, 1929, **470**, 104; 1930, **483**, 132; 1932, **495**, 235; 1934, **511**, 128; 1936, **522**, 56) have proved that position 2 is involved

in xanthate formation, and since soda cellulose is the precursor of xanthate formation, their results are in agreement with those now presented. On the other hand, Piwonka (*Ber.*, 1936, **69**, 1965), by the methylation of a sodium hydroxide cupri-cellulose preparation in the presence of water, appears to have isolated 3-methyl glucosazone. Unless the copper exerts a directive influence, this result is not in agreement with ours and this point is being further investigated.

No evidence is forthcoming as to the entry of a methoxyl residue into the primary alcoholic groups present in cellulose, although both α- and β-methylglucosides and cellobiose (Part III, *loc. cit.*) suffer substitution at this point and the $\cdot CH_2 \cdot OH$ residue is admittedly more reactive than $\cdot CH \cdot OH$. The speculation may be permitted, therefore, that the " secondary valency " forces which are presumed to hold the chains together (Cox, *Ann. Reports*, 1937, **34**, 189) involve the $\cdot CH_2 \cdot OH$ residues. The same argument cannot, however, be applied in the case of amylose, since maltose undergoes substitution both at the secondary hydroxyl residue on C_2 and at the $\cdot CH_2 \cdot OH$ group, although this does not exclude the above possibility.

Experimental.

Potassium Hydroxide–α-Methylglucoside.—α-Methylglucoside [m. p. 164°, $[\alpha]_D^{15°}$ + 155° in water (*c*, 0·5)] (20 g.) in water (10 c.c.) and absolute alcohol (250 c.c.) was mixed with a solution of potassium hydroxide (11 g.) in alcohol (100 c.c.), and dry ether (700 c.c.) added. The mixture was well shaken and kept out of contact with air for 15 mins. The white precipitate was then filtered off rapidly, washed with alcohol (25 c.c.) and ether (25 c.c.), transferred to a porous plate, and dried in a vacuum over phosphoric oxide (Found : KOH, 21·3. $C_7H_{14}O_6$,KOH requires KOH, 22·4%). The analyses of a number of such *products* are recorded below.

Concn. of α-methylglucoside, %	0·93	7·50	5·60	5·00	3·80	3·00	2·50	1·67	1·36
Initial normality of KOH in the glucoside–alkali solution before addition of ether	1·21	0·900	0·550	0·600	0·450	0·360	0·300	0·200	0·165
% KOH in isolated product	20·3	24·0	21·3	22·7	20·4	18·8	19·2	17·6	16·7

Reaction with methyl sulphate. The method previously described was employed, the dry addition compound (20 g.) being stirred with dry neutral methyl sulphate (100 c.c.) for 5 mins. at 60° and for 15 mins. at 75°. After removal of the potassium methyl sulphate, potassium hydroxide (6 g.) in alcohol (40 c.c.) was added until no further precipitation occurred (16 g.); the residue on acetylation yielded a syrup (1·1 g.) which was purified by distillation under 0·05 mm. at 185—195° (bath temp.); yield 0·75 g.; $[\alpha]_D^{16°}$ + 112° in chloroform (*c*, 0·5) (Found : OMe, 17·5; $CH_3 \cdot CO$, 37·5. Calc. for $C_{14}H_{22}O_9$: OMe, 18·6; $CH_3 \cdot CO$, 38·6%).

Isolation of 6-methyl glucosazone. The acetylated syrup (0·7 g.) was deacetylated by Zemplén's method, hydrolysed with 5% hydrochloric acid for 6 hours, the acid neutralised with silver carbonate, the solution evaporated to 10 c.c., and the osazone prepared in the usual manner. Two crops of osazone were isolated and recrystallised from aqueous alcohol; yield 0·1 g., m. p. 182°. The mixed m. p. with 3-methyl glucosazone was 158—162°, but with an authentic specimen of 6-methyl glucosazone there was no depression (Found : OMe, 7·5. Calc. for $C_{19}H_{24}O_4N_4$: OMe, 8·3%).

Potassium Hydroxide–β-Methylglucoside.—The β-methylglucoside tetra-acetate employed had m. p. 104°, $[\alpha]_D^{12°}$ − 18·3° in chloroform (*c*, 0·9). Two methods were used for determining the alkali-combining capacity, the first (Table I) with pure β-methylglucoside, preparation of the addition compound as described above, and analysis, and the second (Table II) with the product obtained by simultaneous deacetylation and compound formation from β-methylglucoside tetra-acetate as previously described for galactose (Part III, *loc. cit.*).

Table I.

Concn. of β-methylglucoside, %	8·50	5·59	5·26	4·19
Initial normality of KOH in the original solution before pptn. with ether	1·51	1·10	0·63	0·25
% KOH in isolated product	18·7	18·6	20·7	21·4

TABLE II.

Concn. of tetra-acetyl β-methylglucoside, %	8·60	4·44	2·80	3·78	3·08	1·57	2·50	4·41
Initial normality of KOH in the original glucoside–alkali solution before addition of ether	1·43	0·887	0·857	0·755	0·615	0·572	0·500	0·463
% KOH in isolated product	18·8	22·2	21·9	22·1	21·4	22·2	21·8	22·5

Potassium hydroxide–β-methylglucoside (22 g.) was prepared by adding to β-methylglucoside (40 g.) mixed with alcohol, potassium hydroxide (40 g.) in alcohol (350 c.c.), followed by ether (1500 c.c.). After 30 mins., the product was treated as before (Found : KOH, 20·2%).

Isolation of 6-methyl glucosazone. Treatment of this product (20 g.) as described above afforded a triacetyl monomethyl β-methylglucoside (1·5 g.), b. p. 180—190° (bath temp.)/0·06 mm., $[\alpha]_D^{18°}$ — 19·4° in chloroform (*c*, 0·9) (Found : OMe, 16·7%). This syrup (1·0 g.) was then deacetylated, hydrolysed, and an osazone prepared. The crude osazone on recrystallisation gave 0·08 g. of product (Found : OMe, 7·5. Calc. for $C_{19}H_{24}O_4N_4$: OMe, 8·3%), m. p. 181°, unchanged on admixture with 6-methyl glucosazone, but depressed to 160—163° on admixture with 3-methyl glucosazone.

Potassium Hydroxide–Maltose.—The alkali-combining capacity of the sugar was determined by both the direct and the indirect titration method and the results described in Part I (*loc. cit.*) were confirmed : *e.g.*, concn. of maltose 1·20% ; normality of KOH, initially 1·37, finally 1·36; KOH combined, 32·2% (indirect), 32·3% (direct). $C_{12}H_{22}O_{11}$,3KOH requires KOH, 33·0%. Maltose (30 g.) was dissolved in water (70 c.c.) and alcohol (500 c.c.), and alcoholic potassium hydroxide (360 c.c. of 1·0N) was added. The *product* (36 g.) isolated in the usual way contained KOH, 29·1%. Methylation was carried out on the above product with dry neutral methyl sulphate for 5 mins. at 65° and for 10 mins. at 70—75°. After removal of potassium methyl sulphate, an excess of N-alcoholic potassium hydroxide was added, followed by ether. The addition compounds so produced were collected and dried. The ethereal filtrate was acidified with acetic acid, and the residue obtained on evaporation was acetylated, yielding a non-reducing syrup (3 g.), $[\alpha]_D^{18°}$ + 103° in chloroform (*c*, 0·5) (Found : OMe, 16·6; CH_3·CO, 35·1. Calc. for $C_{25}H_{38}O_{16}$: OMe, 15·7; CH_3·CO, 36·2%).

Hydrolysis and fractionation of the partly methylated maltose. After deacetylation, this syrup was hydrolysed with 1·5N-sulphuric acid for 6 hours. After neutralisation, evaporation, and extraction with alcohol, a partial fractionation was achieved by the addition of alcoholic potassium hydroxide, yielding a precipitate (A) which was collected and dried (0·9 g.), followed by the addition of dry ether (200 c.c.) to the filtrate to bring about complete precipitation (B) (0·2 g.). The filtrate was neutralised with glacial acetic acid, evaporated, and acetylated. (A) on acidification and treatment with phenylhydrazine yielded glucosazone (mixed m. p.) (OMe, nil). (B) yielded an impure glucosazone (OMe, 2·0%), showing that in an attempt to remove all the free glucose, some methylated glucoses were also precipitated. The syrup (1·3 g.) obtained on acetylation of the residue had $[\alpha]_D^{19°}$ + 52·3° in chloroform (*c*, 0·8) (Found : OMe, 15·9; CH_3·CO, 37·1%). This was evidently a mixture of acetylated mono- and di-methyl glucoses.

Fractionation of the acetylated syrup. Syrups (7·4 g.) from four such experiments were distilled under 0·05 mm. Apart from a small quantity (0·2 g.), b. p. 140—160° (bath temp.) (Found : OMe, 17·5%), the main portion I (4·8 g.) distilled between 155° and 180° (bath temp.) (Found : OMe, 17·5%) and was followed by II (1·7 g.), b. p. 180—230° (bath temp.) (Found : OMe, 9·9%).

Examination of I : *triacetyl dimethyl glucose.* Fraction I was redistilled, yielding a colourless syrup, $[\alpha]_D^{18°}$ + 59° in chloroform (*c*, 0·5) (Found : OMe, 17·5; CH_3·CO, 38·2. Calc. for $C_{14}H_{22}O_9$: OMe, 18·6; CH_3·CO, 38·5%). A portion (1·4 g.) was deacetylated and subjected to osazone formation. The crude osazone, obtained in poor yield, gave 6-methyl glucosazone (0·03 g.) (Found : OMe, 6·9%) on recrystallisation, m. p. 179—181°, unchanged in admixture with an authentic specimen, and m. p. 161° when mixed with 3-methyl glucosazone. The mother-liquors from the recrystallisation were examined for the presence of a dimethyl osazone but none could be detected, and the original reaction solution was extracted with chloroform with the same object but again without success. This result, and in particular the poor yield of osazone, are consistent with the view that the dimethyl glucose carries a methoxyl residue on C_2, and the isolation of 6-methyl glucosazone indicated that the substance was 2 : 6-dimethyl glucose triacetate.

Lactone formation. After deacetylation of the above syrup (1·2 g.) with barium hydroxide and oxidation with bromine at 35° for 60 hours and at 45° for 40 hours until the product was non-reducing, the latter was worked up in the usual way by decomposition of the silver salt of the resulting acid with hydrogen sulphide, and lactonisation at 100°/0·05 mm. for 3 hours gave a colourless syrup (0·5 g.), $[\alpha]_D^{18°}$ + 49° ⟶ + 30·5° after 3 days (Found : OMe, 27·7. Calc. for $C_8H_{14}O_6$: OMe, 30·1%). After treatment with methyl-alcoholic ammonia at 0° for 24 hours, an amide was obtained as a hard glass, $[\alpha]_D^{19°}$ + 52° in water (*c*, 0·4) (Found : OMe, 25·9; N, 6·0. Calc. for $C_8H_{17}O_6N$: OMe, 27·8; N, 6·3%). This amide (0·2 g.) was subjected to the Weerman reaction with sodium hypochlorite and semicarbazide hydrochloride but no hydrazodicarbonamide was formed, indicating substitution on C_2. Gluconamide (0·01 g.) under the same conditions gave hydrazodicarbonamide (0·004 g.).

Examination of fraction II. Further fractionation failed to reduce the methoxyl content (Found : OMe, 10·0. Calc. for a tetra-acetyl monomethyl glucose : OMe, 8·6%), and it was clear that complete separation from the dimethyl glucose had not been effected.

Deacetylation of the syrup (0·7 g.) followed by the usual treatment led to the isolation of an osazone (0·16 g.) devoid of methoxyl; m. p. 199°, not depressed on admixture with glucosazone.

A further portion (0·4 g.) of the syrup was deacetylated with barium hydroxide and converted into the lactone as before (0·2 g.). The slow change in rotation, $[\alpha]_D^{19°}$ + 51° ⟶ + 26° in 4 days (*c*, 0·3, in water), indicated that it was mainly a γ-lactone. This was converted into the amide as before; $[\alpha]_D^{17°}$ + 37° in water (*c*, 0·6) (Found : OMe, 12·8; N, 6·4. Calc. for $C_7H_{15}O_6N$: OMe, 14·8; N, 6·7%). The amide did not give the Weerman reaction.

The precipitates obtained from several experiments, by the addition of ether to the solution after methylation of the original addition compound, removal of potassium methyl sulphate, and addition of alcoholic potassium hydroxide to remove unchanged maltose, were combined and acetylated. A mixture of mono- and di-methyl methylmaltoside acetates (Found : OMe, 12·3%) was obtained, which was hydrolysed, partially fractionated with alcoholic potassium hydroxide, acetylated, distilled, and subjected to osazone formation as above, with the same results.

Potassium Hydroxide–Amylose.—Amylose was prepared from potato starch by the method of Baird, Haworth, and Hirst (J., 1935, 120), the water-soluble product having $[\alpha]_D^{16°}$ + 180° in water (*c*, 0·2). After acetylation with pyridine and acetic anhydride, an acetate was obtained, $[\alpha]_D^{16°}$ + 171° in chloroform (*c*, 0·2) (Found : CH_3·CO, 43·5. Calc. for $C_{12}H_{16}O_8$: CH_3·CO, 44·8%). The alkali-combining capacity was determined by treatment of the acetate with standard alcoholic potassium hydroxide according to the method described in Part III (*loc. cit.*) and the results are recorded below.

Concn. of KOH, N (final)		0·770	0·773	0·446	0·565	0·540	0·390	0·247
KOH, g., required to deacetylate 100 g. of triacetate		62·5	57·6	58·9	53·7	51·0	49·3	46·7
KOH, g., combined with 100 g. of amylose *	Method (1)	27·1	27·2	27·1	29·1	27·1	27·0	28·9
	Method (2)	29·3	30·0	28·9	30·5	30·9	29·4	32·1

* In $(C_6H_{10}O_5,KOH)_x$, 100 g. of amylose are combined with 34·6 g. of KOH.

Preparation of potassium hydroxide–amylose. Amylose acetate (40 g.) suspended in alcohol (175 c.c.) was treated with alcoholic potassium hydroxide (2N, 400 c.c.) and kept for 3 hours. The product (30 g.) was isolated in the usual way [Found : KOH, 23·6. $(C_6H_{10}O_5,KOH)_x$ requires KOH, 25·7%].

Methylation, and examination of the products. Methylation was carried out as previously described. The product (15 g.) remaining after extraction with methyl alcohol was washed with acetone, and extracted with pyridine (300 c.c.) at 65°. To the resulting solution, acetic anhydride (180 c.c.) was added, the mixture kept at 70° for 3 hours and then at room temperature for 2 days, the product being isolated by pouring into water, followed by extraction with chloroform in the usual way. A yellow friable glass (4·2 g.) was obtained, $[\alpha]_D^{16°}$ + 182° in chloroform (*c*, 0·7) (Found : OMe, 2·5; CH_3·CO, 40·3%). This substance was deacetylated, hydrolysed with 1·5N-sulphuric acid, the solution neutralised with barium carbonate, evaporated to dryness, and extracted with alcohol. 2N-Alcoholic potassium hydroxide was added to the extract, the precipitate removed, and dry ether added until no further turbidity was produced. Both precipitates were examined by acidification and treatment with phenylhydrazine acetate : only glucosazone resulted. In a second experiment the dry precipitates were acetylated, and the acetylated syrup from the first precipitate was

found to be devoid of methoxyl, whilst that obtained by the addition of ether contained OMe, 1—2%, so some methylated glucoses were lost. The filtrate after removal of unchanged glucose was acidified with acetic acid, evaporated to dryness, and acetylated, the product (0·5 g.) being distilled as before. A syrup was isolated (0·3 g.), $[\alpha]_D^{18°}$ + 32° in chloroform (*c*, 0·3) (Found: OMe, 8·6. Calc. for $C_{15}H_{22}O_{10}$: OMe, 8·6%). This substance was deacetylated, and on treatment with phenylhydrazine, yielded glucosazone (0·07 g.), m. p. 199°, unchanged on admixture with an authentic specimen (OMe, nil).

The methyl-alcoholic filtrate after the removal of potassium methyl sulphate was treated with excess of 2N-alcoholic potassium hydroxide (100 c.c.), and the precipitation completed by addition of a large volume of dry ether. The filtrate was acidified, evaporated, and acetylated to yield a syrup (1·5 g.), $[\alpha]_D^{18°}$ + 73° in chloroform (*c*, 0·5) (Found: OMe, 12·4; CH_3·CO, 37·7%), the rotation indicating that hydrolysis of the amylose had taken place. This product was deacetylated, hydrolysed, treated with alcoholic potassium hydroxide and ether, and finally acetylated. The precipitated potassium hydroxide complexes yielded exclusively glucosazone on suitable treatment, and acetylation of a portion gave a syrup devoid of methoxyl as expected. The acetylated syrup derived from the filtrate (0·2 g.) had OMe 8·6%, but on deacetylation and osazone formation only glucosazone (0·06 g.) was isolated, thus giving support to the previous result.

Potassium Hydroxide–Cellulose.—The addition product was prepared by the method of Percival, Cuthbertson, and Hibbert (*loc. cit.*) with 35% aqueous potassium hydroxide instead of sodium hydroxide (Found: KOH, 24·1. $C_6H_{10}O_5$,KOH requires KOH, 25·7%). Methylation was carried out on 5 g. at 66° for 15 mins., the liquid decanted, and the product (3·6 g.) washed with acetone and then with water. After drying in the usual way, a white fibrous product was obtained, similar to the original cotton but of a slightly harsher texture. The methoxyl content varied from 5 to 9% for various samples (Calc. for monomethyl cellulose: OMe, 17·6%).

The method of Haworth and Machemer (J., 1932, 2270) was employed to hydrolyse 8 g. of this product (OMe, 9%), and the resulting aqueous solution was subjected to fermentation with yeast for 6 days, then filtered, and evaporated to dryness. The dried residue was converted into glucosides by 5% methyl-alcoholic hydrogen chloride, and the products (3·4 g.) acetylated with pyridine and acetic anhydride. The syrupy acetate was then distilled (0·05 mm.) to yield: fraction I (1·96 g.), b. p. 180—190° (bath temp.); fraction II (0·7 g.), b. p. 190—210° (bath temp.); residue 1·3 g. Fraction I was a colourless syrup and appeared to be a triacetyl monomethyl methylglucoside, $[\alpha]_D^{20°}$ + 77° in chloroform (*c*, 0·5) (Found: OMe, 18·8; CH_3·CO, 38·5. Calc. for $C_{14}H_{22}O_9$: OMe, 18·6; CH_3·CO, 38·6%). It was deacetylated, hydrolysed with 1·5N-sulphuric acid for 6 hours, and the free sugar (0·6 g.) treated with phenylhydrazine in the usual way to yield an osazone (0·1 g.); this was devoid of methoxyl, and had m. p. 200°, unchanged on admixture with glucosazone. Fraction II was a colourless syrup (Found: OMe, 11·3; CH_3·CO, 44·6%), and was tetra-acetyl methylglucoside, contaminated with a little of fraction I, derived from glucose which had escaped fermentation.

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