CLXXXI.—*The Development of a Novel Form of Isomerism in the Sugar Series. Part II. The Third Variety of Tetra-acetyl Methylmannoside.*

By HAROLD GRAHAM BOTT, WALTER NORMAN HAWORTH, and EDMUND LANGLEY HIRST.

THE discussion opened in Part I of this series dealing with the third variety of triacetyl methylrhamnoside (Haworth, Hirst, and Miller, J., 1929, 2469) has now been extended to the anomalous or third variety of tetra-acetyl methylmannoside. The facts are that three forms of tetra-acetyl methylmannoside exist as crystalline substances, and have the following properties (Dale, *J. Amer. Chem. Soc.*, 1924, **46**, 1046):

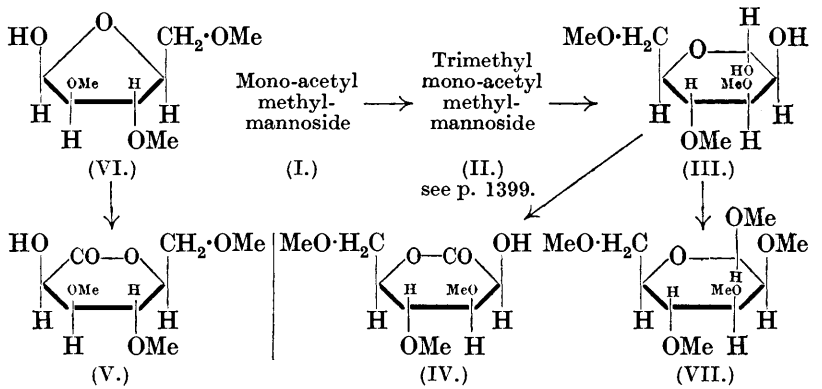
	α-Form.	β-Form.	"γ"-Form.
M. p.	65°	161°	105°
$[\alpha]_D$ in chloroform	+49·1°	−46·8°	−26·6°

In discussing the three corresponding triacetyl methylrhamnosides we were able to recognise all of them as six-atom ring forms of pyranosides. It will now be shown that the α-, β-, and "γ"-forms of tetra-acetyl methylmannoside are also six-atom ring forms, and there arises the question of how the existence of these three modifications can be reconciled with existing views on stereoisomerism in the sugar group. The proof of the constitution of tetra-acetyl α-methylmannoside was developed in an earlier communication (Goodyear and Haworth, J., 1927, 3136), and a similar proof of the pyranose structure of tetra-acetyl β-methylmannoside has been completed and will be published soon.

The third or "γ"-variety of tetra-acetyl methylmannoside possesses several unique features, the most important of which is that three of the acetyl groups are eliminated by contact with cold alkali but the fourth acetyl group is resistant to hydrolysis even with hot alkali. We have submitted the monoacetyl methylmannoside (prepared by an alternative procedure to that given by Levene and Sobotka, *J. Biol. Chem.*, 1926, **67**, 771) to a close investigation, and have found that it behaves in a similar manner to the monoacetyl methylrhamnoside which has already been discussed in Part I of this series. On re-acetylation it passes again to the "γ"-tetra-acetyl methylmannoside, so there can have been no profound change of structure during the partial de-acetylation process. The monoacetyl methylmannoside (I) gave on methylation *monoacetyl trimethyl methylmannoside* (II). The acetyl group in this substance also exhibits the same resistance towards alkaline reagents that was observed in the original tetra-acetate. It is evident that the monoacetyl trimethyl derivative retains the essential structure of the "γ"-tetra-acetyl methylmannoside, a conclusion which is further supported by the ease of hydrolysis of the mannosidic methyl group in either compound with *N*/100-acid in the cold. The trimethyl derivative (II) loses both the mannosidic methyl group and the acetyl group with 2% acid at 100° and yields a crystalline trimethyl mannose which we have designated 3 : 4 : 6-*trimethyl mannopyranose* (III), a sugar which gives rise on oxidation to *d*-3 : 4 : 6-trimethyl δ-mannonolactone (IV), m. p. 96—97°, $[\alpha]_D$ + 167·5° (in water) ⟶ 110°. The corresponding *l*-form (V) of this lactone has already been synthetically prepared by Haworth and Peat from *l*-trimethyl arabofuranose (VI) (J., 1929, 350), and has the same melting point, and the same magnitude of rotation but opposite in sign. From the *d*-lactone the phenylhydrazide of *d*-3 : 4 : 6-trimethyl mannonic acid was prepared, and this again has the same m. p. as that of the phenylhydrazide of the *l*-acid obtained by Haworth and Peat. Since the constitution of the

l-3 : 4 : 6-trimethyl δ-mannonolactone has been proved both by the method of synthesis and by its conversion into the tetramethyl δ-mannonolactone, it will be clear that the *d*-isomeride which has now been isolated must be a six-atom ring form and recognisable under the nomenclature assigned to it in this discussion.

A confirmation of the pyranose structure of the 3 : 4 : 6-trimethyl mannose was developed in the following way. By further methylation the sugar was converted into the crystalline 2 : 3 : 4 : 6-tetramethyl β-methylmannoside (VII) which, in a subsequent publication, will be shown to be capable of hydrolysis to 2 : 3 : 4 : 6-tetramethyl mannopyranose, yielding the characteristic crystalline anilide.



It may be added that the 3 : 4 : 6-trimethyl mannose was crystallised as an α-form mutarotating from $[\alpha]_D = +21° \longrightarrow 8{\cdot}2°$. The rate of hydrolysis of the derived *d*-3 : 4 : 6-trimethyl δ-mannonolactone (IV) was studied and was in full agreement with the values observed by Haworth and Peat (*loc. cit.*) for the *l*-isomeride, but with the sign of rotation reversed. Not only so, but the rate of hydrolysis is comparable with that of *d*-tetramethyl δ-mannonolactone (Drew, Goodyear, and Haworth, J., 1927, 1237).

From these experiments it is inferred that the monoacetyl methylmannoside (I) has the constitution of a six-atom ring form, and that the acetyl group is situated at position 2 of the mannose ring. It is therefore to be formulated as a 2-acetyl derivative of methyl mannopyranoside, and not as a four-atom ring structure as represented by C. S. Hudson (*J. Amer. Chem. Soc.*, 1926, **48**, 1434). The unique behaviour associated with this substance is, however, not explained by this simple formulation, since the tetra-acetyl mannoside from which it was derived differs widely in behaviour from the β-tetra-acetyl methylmannoside, in that from the latter the acetyl group at

position 2 is readily eliminated by hydrolysis along with the other three acetyl groups. There is, therefore, some special character associated with the acetyl group at position 2 in the third variety ("γ") of tetra-acetyl methylmannoside, and it is this remarkable feature which must now receive explanation.

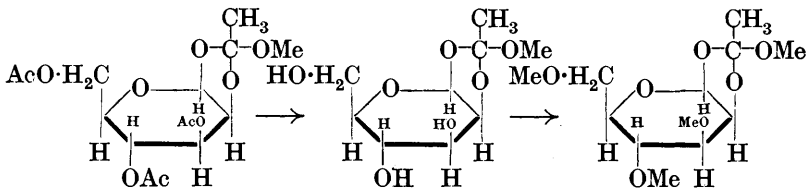
When the above "γ"- or third variety of tetra-acetyl methylmannoside was submitted to methylation with silver oxide and methyl iodide, containing also sodium hydroxide, the product obtained was mainly monoacetyl trimethyl methylmannoside (II) which, on hydrolysis with dilute acid, gave a high yield of crystalline *d*-3 : 4 : 6-trimethyl mannopyranose (IV). On the other hand, the use of excessive quantities of methyl sulphate and alkali effected the replacement of all the acetyl residues by methyl groups, and yielded a mixture of α- and β-forms of tetramethyl methylmannopyranoside from which tetramethyl mannopyranose was afterwards isolated by hydrolysis, and characterised as the crystalline anilide of the latter sugar. The behaviour of the "γ"- or third variety of tetra-acetyl methylmannoside during methylation with these reagents was characteristic. The solution became very dark during the final heating at 100°, and the yield of product was only 40%. Under similar conditions the α- and β-forms of tetra-acetyl methylmannoside give yields which are practically theoretical.

It became evident that, although the replacement of all the four acetyl groups occurred when the "γ"-variety was submitted to this treatment, yet the darkening in colour of the solution was evidence of the intermediate formation of a free sugar, represented by the removal of the mannosidic methyl group simultaneously with the hydrolysis of the acetyl residues. This methyl residue appears to be labile also in contact with dimethylamine and methyl alcohol at 100°.

Still another characteristic feature which clearly differentiates the third or "γ"-variety of the tetra-acetyl or monoacetyl methylmannoside is the ease with which the mannosidic methyl group is hydrolysable with acids of extreme dilution. This property was also remarked upon in the earlier paper dealing with the corresponding rhamnoside. The conclusion there reached was that the resistant acetyl group, which is situated at carbon atom 2 of the pyranose ring, is obstructed by the β-methyl group of the mannoside, and by the proximity of the acetyl group at position 3. It was stated, in the case of the rhamnoside, that this phenomenon might be explicable on the view of the co-ordination of one of the acetoxyl residues with the neighbouring group, and that it was clearly evident that there was restricted movement of the groups attached to carbon atoms, 1, 2, and 3. We suggested as a tentative hypo-

thesis the existence of a strainless ring, which admitted of the interlocking of the groups at carbon atoms 1, 2, and 3.

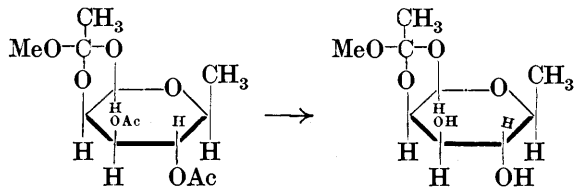
Simultaneously with the work on this problem we have also been conducting an investigation on the transposition or wandering of acetyl residues in the glucose series, and the following paper illustrates the views which we have been led to adopt as an explanation of this phenomenon. The hypothesis introduced by Fischer that the wandering of acyl residues is accompanied by the intermediate formation of an ortho-carbonic ester type of grouping appears to receive confirmation in the case we have studied, and a similar conception of the existence of an ortho-carbonic ester linking seems to us to apply also to the examples of the third or "γ"-varieties of triacetyl methylrhamnoside and tetra-acetyl methylmannoside. The adoption of this view involves both a structural and a stereochemical explanation. The existence of these anomalous compounds, and also the special properties associated with the resistant acetyl group at position 2 in both the rhamnoside and the mannoside, appear to receive a complete explanation from the conclusion that the interlocking of groups at this point in the structure is occasioned by the superposition on the pyranoside structure of a five-atom ring associated through the linking of the groups at carbon atoms 1 and 2.



Third form (obstructed) of *d*-tetra-acetyl methylmannoside.

Obstructed form of *d*-2-acetyl methylmannoside (I).

(II) p. 1397.

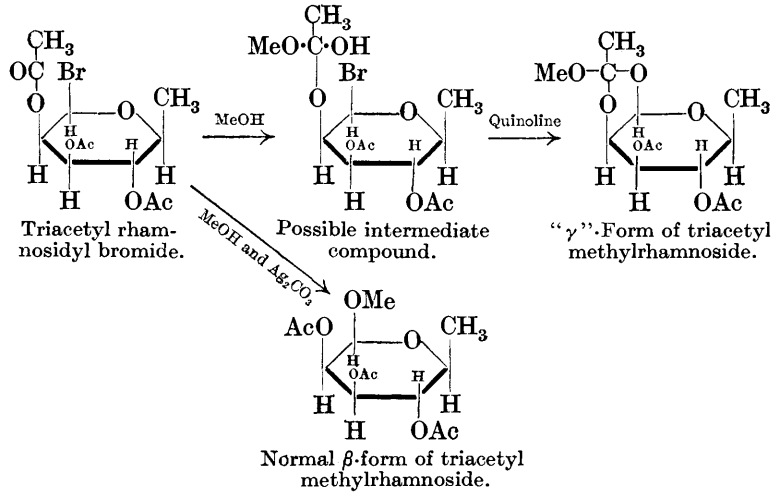


Third (obstructed) form of triacetyl methylrhamnoside.

Obstructed form of *l*-2-acetyl methylrhamnoside.

It must be clearly recognised that the formation of these obstructed forms of methyl-rhamnoside and -mannoside occurs, so far as is at present known, only when the triacetyl rhamnosidyl bromide or tetra-acetyl mannosidyl bromide is submitted to the action of an alcohol in the presence of a base. They do not appear to be formed

by more direct methods. The following scheme may therefore be suggested to explain the mode of formation of these compounds.



(Since it is known that α-glucosidyl bromides yield β-methylglucosides, a process involving a Walden inversion, the bromine atom is here formulated for the sake of clearness as a β-configuration.)

The alternative view that the resistant acetyl residue is located at position 5 of the rhamnose or mannose chain, and that the sugar ring attaches at positions 1 and 2, has not escaped our consideration. But this alternative is rendered very improbable if only for the fact that a mere change of reagent from quinoline to silver carbonate, in the transformation from the bromide to the rhamnoside, produces a substantial yield of the ordinary unobstructed form of triacetyl β-methylrhamnoside to which has been allocated the pyranose structure.

This formulation for the third varieties of the rhamnoside and mannoside as ortho-carbonic ester derivatives would seem also to provide a reason for the ease with which they undergo hydrolysis with dilute acid when compared with the much greater resistance of the α- and β-forms to these reagents.

During the preparation of the present paper for the press a communication was received from Professor Freudenberg informing us that he had reached, independently, the same conclusion as ourselves as to the structure herein assigned to the "γ"-triacetyl methylrhamnoside, and that a preliminary note by Freudenberg and Braun on this subject was to appear in *Naturwissenschaften*, May 1, 1930.

EXPERIMENTAL.

Preparation of "γ"-Monoacetyl Methylmannoside.—Penta-acetyl mannose was obtained as a liquid containing both the α- and the β-form by treating mannose with acetic anhydride and pyridine at 0° for 4 days. The product was isolated by the method used by Haworth, Hirst, and Miller (*loc. cit.*) for rhamnose tetra-acetate. Tetra-acetyl mannosidyl bromide was then prepared from the liquid penta-acetyl mannose and was converted into "γ"-tetra-acetyl methylmannoside by Dale's method (*loc. cit.*). The latter substance was repeatedly crystallised from ether until it had m. p. 104°, and $[\alpha]_D^{20°} - 27°$ in chloroform, in agreement with the constants recorded by Dale.

The following method was found to be more convenient than the one given by Levene and Sobotka (*loc. cit.*) for the transformation of "γ"-tetra-acetyl methylmannoside into monoacetyl methyl-mannoside. A solution of the former substance in an excess of *N*/2-alcoholic sodium hydroxide was kept at 0° for 16 hours. After neutralisation by carbon dioxide the solution was filtered and then evaporated to dryness under diminished pressure at 40°. The residue was extracted several times with cold ethyl acetate. Removal of the solvent under diminished pressure at 40° left a viscid syrup, which was obtained as a hygroscopic powder after prolonged drying in a vacuum (yield, 72% of the theoretical). $[\alpha]_D^{24°} - 6°$ (*c*, 0·83 in water) (Found: C, 46·0; H, 7·1; OMe, 11·2. Calc. for $C_9H_{16}O_7$: C, 45·8; H, 6·8; OMe, 13·2%).

Monoacetyl γ-methylmannoside was non-reducing and the acetyl group resisted hydrolysis by 15% aqueous sodium hydroxide at 80°. The substance was, however, readily hydrolysed by dilute acids with loss of methyl and acetyl groups.

Acetylation of Monoacetyl Methylmannoside.—A solution of mono-acetyl methylmannoside (2 g.) in pyridine (15 c.c.) and acetic anhydride (21 c.c.) was kept at − 5° for 50 hours, and then poured into water. The product was extracted by chloroform, the chloro-form solution was neutralised by shaking with aqueous sodium bicarbonate and dried, and the solvent was then removed by distillation under diminished pressure at 35°. After removal of the pyridine by distillation in steam at 35°/11 mm., "γ"-tetra-acetyl methylmannoside was obtained as a colourless crystalline mass (3 g.), m. p. 100°. After recrystallisation from ether the m. p. was 102°. A mixed m. p. determination with an authentic specimen showed no depression. $[\alpha]_D^{20°} - 26·9°$ (*c*, 1·11 in chloroform) (Found: C, 49·5; H, 6·2; OMe, 8·3. Calc. for $C_{15}H_{22}O_{10}$: C, 49·7; H, 6·1; OMe, 8·6%).

Methylation of Monoacetyl Methylmannoside.—(a) *By means of*

silver oxide and methyl iodide. A solution of monoacetyl methylmannoside (7 g.) in methyl alcohol (7 c.c.) and methyl iodide (70 c.c.) was heated at 30° with silver oxide (20 g.) until the reaction had commenced, and this proceeded for some time without further heating. Silver oxide was added from time to time (70 g. in all) and the temperature was gradually raised to 45°. At the end of 6 hours the product was extracted by chloroform and after isolation was remethylated in the usual way with silver oxide (30 g.) and methyl iodide (30 c.c.). It was then distilled, giving *monoacetyl trimethyl methylmannoside* (6·3 g.) as a colourless liquid, b. p. about 120°/0·1 mm.; $n_D^{15°}$ 1·4594; $[\alpha]_D^{23°}$ −20° (*c*, 1·24 in water); $[\alpha]_D^{23°}$ −11° (*c*, 1·0 in chloroform) (Found: C, 51·8; H, 8·1; OMe, 42·0. $C_{12}H_{22}O_7$ requires C, 51·8; H, 7·9; OMe, 44·7%).

(b) *By means of methyl sulphate.* Monoacetyl methylmannoside (5 g.), dissolved in acetone (30 c.c.) and water (10 c.c.), was treated at 50° with methyl sulphate (50 c.c.) and 30% aqueous sodium hydroxide (150 c.c.), the solution being maintained strongly alkaline throughout. (During the methylation there is a tendency for the formation of coloured decomposition products, and it is desirable to omit the usual heating for one hour at 90—100° at the end of the reaction.) The product (2·5 g.), which was isolated in the usual way, had b. p. about 120°/0·1 mm., $n_D^{18°}$ 1·4582, $[\alpha]_D^{22°}$ −23° (*c*, 1·0 in water). The identity of this material with the monoacetyl trimethyl methylmannoside described above was established by the conversion of both into the same crystalline trimethyl mannose, the yield in each case being over 90% of the theoretical.

The acetyl group in monoacetyl trimethyl "γ"-methylmannoside resisted hydrolysis by aqueous sodium hydroxide, no measurable amount of acetic acid being liberated during 50 hours when a solution of the substance in 3% aqueous alkali was kept at 15°. During this period the specific rotation remained unaltered. In hot aqueous alkali monoacetyl trimethyl "γ"-methylmannoside was slightly unstable, as was shown by the formation of coloured decomposition products. Fehling's solution was reduced to a small extent after prolonged boiling. The amount of decomposition was, however, minute even after treatment with 3% aqueous sodium hydroxide at 50° for 2 hours, since under these conditions 0·191 g. of substance accounted for only 0·2 c.c. of alkali. Further evidence of decomposition in the presence of alkali was provided by the marked development of colour during the simultaneous deacetylation and methylation of monoacetyl trimethyl "γ"-methylmannoside by means of methyl sulphate and strong alkali (see below).

Monoacetyl trimethyl methylmannoside was extremely sensitive to dilute hydrochloric acid. The specific rotation in *N*/100-acid at

20° changed in 60 minutes from $[\alpha]_D^{20°}$ — 25° to the constant value + 2°. The liquid then vigorously reduced warm Fehling's solution. $[\alpha]_D^{20°}$ — 20° (4 mins.); — 13° (10 mins.); — 6·4° (20 mins.); — 1·6° (30 mins.); + 0·4° (45 mins.); 2° (60 mins.; constant value). No acetic acid was liberated during this period, since a solution of 0·1889 g. of substance in 26·8 c.c. of *N*/100-hydrochloric acid required for neutralisation after 60 minutes 27·0 c.c. of *N*/100-sodium hydroxide. Complete hydrolysis of the acetyl group would involve the liberation of acetic acid equivalent in this case to an additional 68·2 c.c. of *N*/100-alkali. The removal of the acetyl group was effected by the use of *N*/2-sulphuric acid at 90° for 60 minutes (Found : $CH_3{\cdot}CO$, 14·0. Calc., 15·5%).

3 : 4 : 6-*Trimethyl Mannopyranose.*—The following series of experiments was carried out in duplicate with material obtained respectively by methods (a) and (b) of the preceding section. The products were identical, and it is only necessary, therefore, to describe one set of experiments.

Monoacetyl trimethyl methylmannoside was dissolved in *N*/2-hydrochloric acid and heated on the water-bath for 90 minutes. The solution was neutralised with barium carbonate, filtered, and evaporated to dryness under diminished pressure. The product was extracted with chloroform and distilled, giving 3 : 4 : 6-trimethyl mannopyranose as a syrup, b. p. about 135°/0·04 mm., $n_D^{16°}$ 1·4734. This soon crystallised and, on recrystallisation from ether, d-3 : 4 : 6-*trimethyl α-mannopyranose* was obtained, m. p. 101—102°, $[\alpha]_D^{22°}$ + 36° (*c*, 0·8 in methyl alcohol), $[\alpha]_D^{22°}$ +21° (*c*, 1·04 in water; initial value). Yield, 90% of the theoretical (Found : C, 48·7; H, 8·3; OMe, 40·9. $C_9H_{18}O_6$ requires C, 48·7; H, 8·1; OMe, 41·8%).

The mutarotation of 3 : 4 : 6-trimethyl mannopyranose in aqueous solution at 22° was complete in about 90 minutes, the equilibrium value being $[\alpha]_D^{22°}$ + 8·2° : $[\alpha]_D^{22°}$ + 19° (3 mins.); 18·5° (5 mins.); 11·5° (30 mins.); 10° (45 mins.); 8·2° (90 mins., constant value). From these figures the initial value was obtained by extrapolation.

3 : 4 : 6-Trimethyl mannopyranose (1·0 g.) was methylated by means of methyl iodide (30 c.c.) and silver oxide (10 g.), the addition of methyl alcohol (2 c.c.) being necessary to effect solution. The mixture was heated at 35° for 3 hours and then allowed to boil gently for an additional 4 hours. The product, after being re-methylated in the usual way, crystallised (yield, 0·95 g.). On distillation crystalline tetramethyl β-methylmannopyranoside was obtained mixed with 12% of the α-isomeride, b. p. about 90°/0·04 mm., $n_D^{19°}$ 1·4521 (supercooled liquid), $[\alpha]_D^{20°}$ — 65° (*c*, 0·7 in water). Recrystallisation from light petroleum (b. p. 40—60°) gave pure tetramethyl β-methylmannopyranoside as long needles, m. p.

36—37°, alone or when mixed with an authentic specimen, $[\alpha]_D^{24°} - 78°$ (*c*, 0·4 in water).

d-3 : 4 : 6-*Trimethyl* δ-*Mannonolactone*.—3 : 4 : 6-Trimethyl mannopyranose (3·7 g.) was dissolved in water (25 c.c.) and treated at 35—40° with bromine (4·5 c.c.) for 2 days; the solution was then found to be non-reducing. After removal of the remaining bromine by aeration the solution was neutralised with silver oxide, the organic acid liberated from its silver salt by titration with hydrochloric acid, the water removed by distillation under diminished pressure, and the product dissolved in ether in order to remove a small quantity of inorganic matter. Evaporation of the ether left crystalline *d*-3 : 4 : 6-trimethyl δ-mannonolactone (3·2 g.) which, after recrystallisation from ether, had m. p. 96—97°, $[\alpha]_D^{19°} + 167·5°$ (*c*, 0·7 in water). These constants are in excellent agreement with those recorded by Haworth and Peat for the corresponding *l*-3 : 4 : 6-trimethyl δ-mannonolactone (*loc. cit.*), which has m. p. 96—97° and $[\alpha]_D - 167°$.

The phenylhydrazide of *d*-3 : 4 : 6-trimethyl mannonic acid was prepared by heating the lactone (0·2 g.) with the calculated quantity of phenylhydrazine in benzene solution for 30 minutes on the water-bath. The product (0·3 g.) crystallised completely and had m. p. 137—139°, unaltered by recrystallisation from benzene. The m. p. of the *l*-isomeride is 137—139°.

The hydrolysis of the lactone in aqueous solution was followed polarimetrically: $[\alpha]_D^{20°} + 167·5°$ (5 mins.); 167° (30 mins.); 162° (1·5 hrs.); 154° (4·5 hrs.); 147° (8 hrs.); 125° (24·5 hrs.); 118° (32 hrs.); 110° (74 hrs., constant value). If the sign of rotation be reversed, these figures are in excellent agreement with those recorded by Haworth and Peat for the *l*-isomeride.

The rotation of the acid in aqueous solution was measured in the manner described in previous papers: $[\alpha]_D^{20°} + 31°$ (*c*, 0·7, calc. as lactone; initial value); 39° (1 hr.); 62° (4·5 hrs.); 103° (23 hrs.); 107° (30 hrs.); 111° (48 hrs., constant value). The proportion of lactone present at equilibrium was therefore 58%.

Attempted Simultaneous Deacetylation and Methylation of "γ"-Tetra-acetyl Methylmannoside by Means of Methyl Iodide and Silver Oxide in the Presence of Solid Sodium Hydroxide.—Silver oxide (70 g.) and solid sodium hydroxide (6 g.) were added to a solution of "γ"-tetra-acetyl methylmannoside (10 g.) in methyl iodide (50 c.c.). The mixture was heated at 45° for 8 hours. The product (9 g.) was extracted by chloroform and subjected to a second treatment under similar conditions, and was then distilled, giving a colourless viscid syrup (6 g.), b. p. about 120°/0·1 mm., $n_D^{16°}$ 1·4601, $[\alpha]_D^{19°} - 16°$ in chloroform (Found: C, 51·8; H, 8·5; OMe, 45·1%). The material

was therefore mainly monoacetyl trimethyl methylmannoside, and the correctness of this view was proved by hydrolysis with *N*/5-hydrochloric acid at 95°. During 2 hours the specific rotation altered from $[\alpha]_D^{20°}$ — 7° to + 4°. The product, which was isolated in the usual way, was 3 : 4 : 6-trimethyl mannopyranose, m. p. 101° (yield, 90%).

Similar experiments with silver oxide and solid sodium hydroxide were carried out on monoacetyl trimethyl methylmannoside, but in no case could the acetyl group be removed, and the monoacetyl trimethyl methylmannoside was recovered unchanged.

Simultaneous Deacetylation and Methylation by Means of Methyl Sulphate and Alkali.—"γ"-Tetra-acetyl methylmannoside (5·5 g.), dissolved in acetone (15 c.c.), was treated at 50° with a large excess of methyl sulphate (55 c.c.) and 30% aqueous sodium hydroxide (140 c.c.). During the final heating at 100° for 1 hour the solution became very dark. The product was methylated three times by Purdie's reagents and distilled, giving a colourless liquid, b. p. about 85°/0·03 mm., $n_D^{17°}$ 1·4530, $[\alpha]_D^{20°}$ — 15° (*c*, 0·9 in water), $[\alpha]_D^{22°}$ — 7° (*c*, 0·7 in chloroform). Yield, 40% (Found : OMe, 58·2. Calc. for the tetramethyl methylmannoside, 62%). During hydrolysis with 6% hydrochloric acid at 80° the specific rotation altered from $[\alpha]_D^{20°}$ — 15° to the constant value $[\alpha]_D^{20°}$ + 14°. The product was a syrup which, when boiled with aniline in ethyl-alcoholic solution, gave tetramethyl mannopyranose anilide, m. p. 140—142°, alone or in admixture with an authentic specimen. The overall yield of syrupy tetramethyl mannopyranose from "γ"-tetra-acetyl methylmannoside was 25% of the theoretical, and the minimum yield of crystalline anilide from the tetramethyl mannopyranose was 70%.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[*Received, May 19th*, 1930.]