

101. *The Reaction of Magnesium Halides with  $\alpha\beta$ -Anhydro-sugars.*

By G. N. RICHARDS, L. F. WIGGINS, and W. S. WISE.

The reaction of  $\alpha\beta$ -anhydro-sugars with magnesium halides has been studied in ethereal and in aqueous solution. Derivatives of 3-deoxy-3-iodo-, 3-bromo-3-deoxy-, and 3-chloro-3-deoxy- $\alpha$ -D-altroside, of 2-chloro-2-deoxy-, 2-bromo-2-deoxy-, and 2-deoxy-2-iodo- $\alpha$ -D-altroside, and of 3-chloro-3-deoxy- and 3-deoxy-3-iodo- $\alpha$ -D-glucoside have been obtained by the reaction of magnesium halides with 2 : 3-anhydro-derivatives of methyl  $\alpha$ -D-mannoside and -alloside in ether or tetrahydropyran. Magnesium chloride reacts rapidly with  $\alpha\beta$ -anhydro-sugars in aqueous solution in the presence of dilute hydrochloric acid. This reaction provides a diagnostic test for  $\alpha\beta$ -anhydro-sugars or  $\alpha\beta$ -anhydrides of sugar alcohols.

WHEN  $\alpha\beta$ -anhydro-sugar derivatives are treated with Grignard reagents in ether or tetrahydropyran solution, the main products are halogeno-sugar compounds. Newth, Richards, and Wiggins (*J.*, 1950, 2336), and Richards and Wiggins (*J.*, 1953, 2442), however, found that when methyl 2 : 3-anhydro-4 : 6-di-*O*-methyl- $\alpha$ -D-alloside was treated with methylmagnesium iodide a *C*-methyl derivative was also formed. It therefore seemed probable that  $\alpha\beta$ -anhydro-sugars react with Grignard reagents through the magnesium dialkyls and magnesium halides which are formed therefrom, the first giving rise to *C*-alkyl compounds and the second to halogeno-sugars. Thus, it seemed worth while to study separately the reactions of magnesium dialkyls and magnesium halides with  $\alpha\beta$ -anhydro-sugars. The work reported in this paper is on the reaction with magnesium halides.

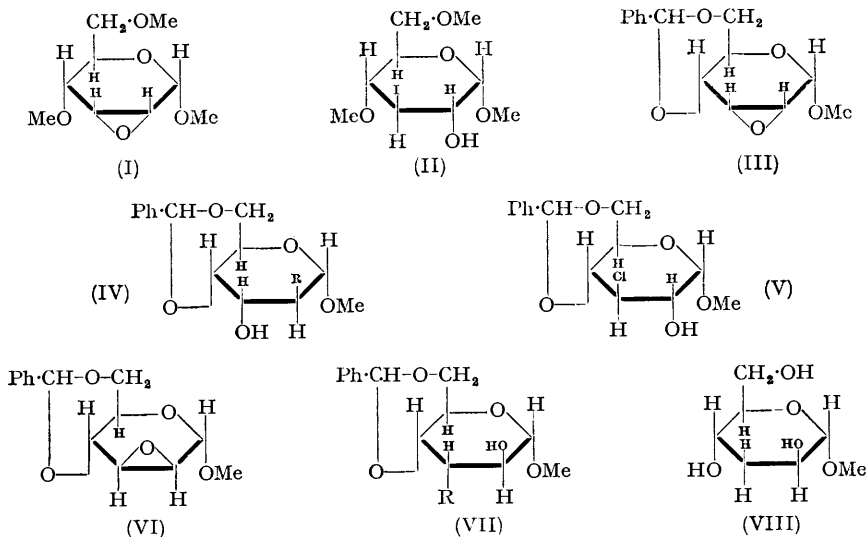
The anhydro-sugars used were the 4 : 6-*O*-benzylidene derivatives of methyl 2 : 3-anhydro- $\alpha$ -D-alloside and -mannoside. Newth, Richards, and Wiggins (*loc. cit.*) had found that methyl 2 : 3-anhydro-4 : 6-di-*O*-methyl- $\alpha$ -D-alloside (I) with a suspension of anhydrous magnesium iodide in ether gave a 45% yield of methyl 3-deoxy-3-iodo-4 : 6-di-*O*-methyl- $\alpha$ -D-glucoside (II) identical with the compound obtained by reaction of methylmagnesium iodide with the same anhydro-sugar. In the latter reaction, however, the 3-deoxy-3-iodo-glucoside was obtained in only 5.8% yield and other products, including a *C*-methyl sugar and a derivative of 2-deoxy-2-iodoaltroside, were also obtained.

Methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene- $\alpha$ -D-alloside (III) behaved somewhat differently with magnesium iodide. It reacted slowly in diethyl ether but faster when the mixture was heated with an ether of higher boiling point, namely, tetrahydropyran. The product was a crystalline iodo-sugar (59% yield), identical with the methyl 4 : 6-*O*-benzylidene-2-deoxy-2-iodo- $\alpha$ -D-altroside (IV; R = I) previously isolated by Richards and Wiggins (*loc. cit.*) from the reaction of ethylmagnesium iodide with the same alloside (III). Similarly, when the compound (III) was treated in tetrahydropyran with anhydrous magnesium bromide or chloride, the corresponding 2-bromo-2-deoxy- (IV; R = Br) and 2-chloro-2-deoxy-altroside (IV; R = Cl) were isolated in 32% and 18% yield respectively. Reaction of magnesium chloride in tetrahydropyran at 120° in a sealed tube gave a slightly higher yield (23%) of methyl 4 : 6-*O*-benzylidene-2-chloro-2-deoxy- $\alpha$ -D-altroside (IV; R = Cl) but, in addition, methyl 4 : 6-*O*-benzylidene-3-chloro-3-deoxy- $\alpha$ -D-glucoside (V) (Newth, Overend, and Wiggins, *J.*, 1947, 10) in 3% yield. The structure (IV; R = Cl) was confirmed by hydrolysis of the compound by oxalic acid in aqueous acetone to methyl 2-chloro-2-deoxy- $\alpha$ -D-altroside (Newth, Overend, and Wiggins, *loc. cit.*).

The experiments with magnesium halides and the alloside (III) were repeated with a close analogue, methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene- $\alpha$ -D-mannoside (VI). This compound also did not react with magnesium iodide in diethyl ether, but in boiling tetrahydropyran solution gave only (33%) methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (VII; R = I), the structure of which was established as follows: (i) Reductive dehalogenation with Raney nickel in alcohol afforded methyl 3-deoxy- $\alpha$ -D-mannoside (VIII), m. p. 123—124°,  $[\alpha]_D^{25} +129.6^\circ$ . Bollinger and Prins (*Helv. Chim. Acta*, 1946, 29, 1061) described it as amorphous, showing  $[\alpha] +108.9^\circ \pm 2^\circ$ , the discrepancy probably

being due to the impurity of this material. (ii) When the iodide (VII; R = I) was treated with methyl iodide and silver oxide under anhydrous conditions in an attempt to prepare the 2-methyl ether it was transformed into methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene- $\alpha$ -D-mannoside. (iii) The product (VIII) of reductive dehalogenation was not oxidised by lead tetra-acetate in acetic acid.

With magnesium bromide in tetrahydropyran, the mannoside (VI) afforded methyl 4 : 6-*O*-benzylidene-3-bromo-3-deoxy- $\alpha$ -D-altroside (VII; R = Br), converted by Raney nickel in alcohol into the same methyl 3-deoxy- $\alpha$ -D-mannoside (VIII) as was obtained from the 3-deoxy-3-iodoaltroside (VII; R = I), which proves the structure of the 3-bromide. Anhydrous magnesium chloride and the mannoside (VI) did not react in boiling tetrahydropyran and, although the starting material was consumed at 140° under pressure, the only product isolated was a chlorine-containing syrup.



Thus, with both the anhydroalloside (III) and the anhydromannoside (VI) reactivity towards magnesium halides decreases in the order  $I > Br > Cl$ . It might have been expected that such salts as lithium chloride or zinc chloride would have reacted with the anhydro-sugars but in neither case could products other than original starting materials be recovered; it must be inferred that lithium and zinc chloride are less reactive than magnesium chloride towards  $\alpha\beta$ -anhydro-sugars in ether.

The relative ease of fission of the epoxide ring in anhydro-sugars by magnesium halides in ether and the known fission of ethylene oxide itself in water in the presence of high concentrations of halide ions with formation of ethylene halogenohydrins (Bronsted, Kilpatrick, and Kilpatrick, *J. Amer. Chem. Soc.*, 1929, 51, 428) led us to examine their reaction with magnesium salts in aqueous solution.

Peat and Wiggins (*J.*, 1938, 1088) had shown that cold 5% hydrochloric acid did not open the oxide ring of methyl 2 : 3-anhydro-4 : 6-di-*O*-methyl- $\alpha$ -D-alloside (I) although at 95° it caused both ring fission and hydrolysis of the methyl glucoside group. However, the same anhydro-sugar derivative in cold 0.5*N*-hydrochloric acid saturated with magnesium chloride very rapidly gave a crystalline chlorodeoxy-4 : 6-di-*O*-methylhexoside. This was the 4 : 6-di-*O*-methyl derivative of either methyl 2-chloro-2-deoxy- $\alpha$ -D-altroside or 3-chloro-3-deoxy- $\alpha$ -D-glucoside. Hydrolysis led to the corresponding chlorodeoxy-sugar which, because it reacted with 1 mol. of sodium metaperiodate, is accorded the glucose structure. 2-Chloro-2-deoxy-4 : 6-di-*O*-methylaltrose would not have been expected to react with sodium metaperiodate.

In this reaction of  $\alpha\beta$ -anhydro-sugars with dilute hydrochloric acid saturated with

magnesium chloride, hydrogen chloride is consumed. The reaction can therefore be followed by titration with alkali. Methyl 2 : 3-anhydro-4 : 6-di-*O*-methyl- $\alpha$ -*D*-alloside when treated at room temperature with 0.5*N*-hydrochloric acid saturated with magnesium chloride consumes 98% of the theoretical amount of alkali in 15 min. A selection of sugar and sugar alcohol anhydrides was treated similarly, with the results shown in the accompanying Table. The reaction appears to be diagnostic for  $\alpha\beta$ -anhydro-sugars as well as offering a method of preparation of halogeno-sugars.

Anhydride	Alkali consumed in 15 min. (% theor. for 1 anhydro-ring)
Methyl 2 : 3-anhydro-4 : 6-di- <i>O</i> -methyl- $\alpha$ - <i>D</i> -alloside .....	98
5 : 6-Anhydro-1 : 2- <i>isopropylidene</i> glucofuranose .....	87 (0 *)
1 : 4-3 : 6-Dianhydro-2 : 5-di- <i>O</i> -methylsorbitol .....	0
1 : 6-3 : 4-Dianhydro- $\beta$ - <i>D</i> -mannose .....	93
1 : 5-Anhydromannitol (styracitol) .....	0

\* No magnesium chloride added.

### EXPERIMENTAL

*Reaction of Methyl 2 : 3-Anhydro-4 : 6-O-benzylidene- $\alpha$ -D-alloside with Anhydrous Magnesium Halides.*—(a) *Magnesium iodide.* (i) The alloside was extracted from the thimble of a Soxhlet apparatus by boiling anhydrous ether into ether containing an excess of anhydrous magnesium iodide (cf. Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197, for this method in connection with lithium aluminium hydride). After 1 hour's refluxing the starting material (96%) was recovered as described below. (ii) The alloside (0.510 g.) was heated under reflux for 2 hr. with anhydrous tetrahydropyran (20 c.c.) and magnesium iodide (1.5 g.). The solution was cooled to room temperature, and water (20 c.c.) added, followed by slight excess of dilute hydrochloric acid to dissolve the precipitated magnesium hydroxide. The tetrahydropyran solution was separated, washed with sodium hydrogen carbonate and sodium thiosulphate solutions and with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to dryness. The residue crystallised on inoculation and, recrystallised from ethanol, gave methyl 4 : 6-*O*-benzylidene-2-deoxy-2-iodo- $\alpha$ -*D*-altroside (0.445 g., 59%), cubes, m. p. 105—106° alone or in admixture with an authentic sample (Richards and Wiggins, *J.*, 1953, 2442).

(b) *Magnesium bromide.* The alloside (0.504 g.) and anhydrous magnesium bromide (1.4 g.) were heated under reflux for 2½ hr. with anhydrous tetrahydropyran (20 c.c.) with stirring. The mixture, treated in the usual way, yielded a yellow syrup which, on trituration with ether and light petroleum, yielded methyl 4 : 6-*O*-benzylidene-2-bromo-2-deoxy- $\alpha$ -*D*-altroside (0.34 g., 52%). When recrystallised from ethanol, this had m. p. and mixed m. p. 117.5—118.5°.

(c) *Magnesium chloride.* (i) The alloside (1.01 g.) was heated with tetrahydropyran (40 c.c.) and anhydrous magnesium chloride (0.72 g.) under reflux and stirred for 2 hr., then cooled to room temperature. Water (20 c.c.) was added. The precipitated crystalline solid (0.6 g.), when separated at the centrifuge, washed with water, and dried, had m. p. 199—200° alone or in admixture with starting material. The tetrahydropyran layer was separated, washed as in (a), dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated to dryness. The white crystalline residue was extracted with ethanol (30 c.c.) at room temperature and the insoluble portion separated; this was unchanged starting material (0.18 g.), m. p. 197—199°. The extract was evaporated to dryness and the residue crystallised by trituration with ether. After recrystallisation from ethyl acetate-light petroleum (b. p. 60—80°), methyl 4 : 6-*O*-benzylidene-2-chloro-2-deoxy- $\alpha$ -*D*-altroside (0.162 g., 14%) had m. p. 102—103.5°,  $[\alpha]_D^{25} +88.4^\circ$  (c, 1 in  $\text{CHCl}_3$ ) (Found: C, 55.7; H, 5.5.  $\text{C}_{14}\text{H}_{17}\text{O}_5\text{Cl}$  requires C, 55.9; H, 5.7%).

(ii) The alloside (1.04 g.), tetrahydropyran (30 c.c.), and anhydrous magnesium chloride (1 g.) were heated at 120° for 10 hr. in a sealed glass tube. Some insoluble amorphous brown material had then appeared. Water, followed by dilute hydrochloric acid, was added and the tetrahydropyran layer washed and dried as above. On evaporation of the solvent a brown amorphous residue remained which was dissolved in ether (4 c.c.) and light petroleum (4 c.c.; b. p. 60—80°) and chromatographed on alumina (40 × 1 cm.). Elution with ether-light petroleum (1 : 5) gave as first fraction a yellow liquid (0.348 g.) having a strong odour of benzaldehyde; it seemed probable that this material contained decomposition products formed by the prolonged heating and it was not further investigated. Elution with the same mixed solvents gave as second fraction methyl 4 : 6-*O*-benzylidene-2-chloro-2-deoxy- $\alpha$ -*D*-altroside

(0.296 g. 25.1%) which, crystallised under ether and recrystallised from ethanol, had m. p. and mixed m. p. 102—103°. A later fraction yielded 48 mg. of methyl 4 : 6-O-benzylidene-3-chloro-3-deoxy- $\alpha$ -D-glucoside which, recrystallised from ethyl acetate–light petroleum (b. p. 60—80°), had m. p. 164—165°,  $[\alpha]_D^{25} + 51.5^\circ$  (c, 1.5 in  $\text{CHCl}_3$ ) (Found: C, 56.0; H, 5.4. Calc. for  $\text{C}_{14}\text{H}_{17}\text{O}_6\text{Cl}$ : C, 55.9; H, 5.7%) (cf. Newth, Overend, and Wiggins, *loc. cit.*).

*Treatment of Methyl 4 : 6-O-Benzylidene-2-chloro-2-deoxy- $\alpha$ -D-altroside with Toluene-*p*-sulphonyl Chloride.*—The altroside (89 mg.) in dry pyridine (2 c.c.), treated with toluene-*p*-sulphonyl chloride (0.2 g.) at room temperature for 18 hr., gave the 3-toluene-*p*-sulphonate, m. p. 153—153.5° (from ethanol–water),  $[\alpha]_D^{25} + 43.6^\circ$  (c, 1 in  $\text{CHCl}_3$ ) (Found: C, 55.5; H, 5.1.  $\text{C}_{21}\text{H}_{23}\text{O}_7\text{ClS}$  requires C, 55.4; H, 5.1%).

*Hydrolysis of Methyl 4 : 6-O-Benzylidene-2-chloro-2-deoxy- $\alpha$ -D-altroside with Oxalic Acid.*—A solution of the altroside (0.184 g.) in acetone (15 c.c.) was heated with aqueous oxalic acid (0.6 g. of the dihydrate in 2 c.c. of water), the optical rotation changing from  $[\alpha]_D^{25} + 88.7^\circ$  (initial) to  $+77.6^\circ$  (4.5 hr., const.). Then the solution was neutralised with barium carbonate and filtered and the filtrate evaporated to dryness. The residue was steam-distilled until free from benzaldehyde and again evaporated to dryness, and this residue was taken up in water. The solution was filtered and evaporated to a colourless syrup which crystallised readily on trituration with ethyl acetate. Recrystallised from the same solvent, methyl 2-chloro-2-deoxy- $\alpha$ -D-altroside (0.057 g., 44%) had m. p. and mixed m. p. 161—162° (Newth, Overend, and Wiggins, *loc. cit.*). By the procedure of Hockett and McClenahan (*J. Amer. Chem. Soc.*, 1939, 61, 1667) a solution of the altroside (57.0 mg.) in glacial acetic acid (50 c.c.) consumed 1.02 mols. of lead tetra-acetate in 1 hr. at room temperature.

*Reaction of Methyl 2 : 3-Anhydro-4 : 6-O-benzylidene- $\alpha$ -D-mannoside with Anhydrous Magnesium Halides.*—(a) *Magnesium iodide.* The anhydromannoside (0.519 g.), anhydrous magnesium iodide (1.5 g.), and tetrahydropyran (20 c.c.) were heated under reflux for 3 hr., then cooled and water (20 c.c.) was added. The solution was then acidified, and the ethereal layer separated, washed in the usual way, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated. Fractional recrystallisation of the residue from ethanol–water yielded methyl 4 : 6-O-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (0.257 g., 33.3%), m. p. 163—163.5°,  $[\alpha]_D^{25} + 111^\circ$  (c, 4 in  $\text{CHCl}_3$ ) (Found: C, 43.2; H, 4.45.  $\text{C}_{14}\text{H}_{17}\text{O}_5\text{I}$  requires C, 42.85; H, 4.4%). Some starting material (0.221 g., 42.6%) was also recovered.

When the same experiment was carried out in boiling ether solution for 4 hr., no reaction occurred and 99% of the anhydromannoside was recovered.

(b) *Magnesium bromide.* A solution of the anhydromannoside (1.03 g.) in tetrahydropyran (30 c.c.) was heated under reflux for 2 hr. with anhydrous magnesium bromide (3 g.). An amorphous white precipitate separated. After the mixture had been cooled to room temperature, water (30 c.c.) was added, followed by a slight excess of dilute hydrochloric acid, and the ethereal phase washed and dried in the usual manner before being evaporated to a yellow syrup with a characteristic sweet odour. This was dissolved in a mixture of ether (2 c.c.) and light petroleum (2 c.c.; b. p. 60—80°) and chromatographed on alumina (30 × 1 cm.). Elution with ether–light petroleum (1 : 5) gave as first fractions optically inactive, unidentified mixtures (0.483 g.). Later fractions from the same eluant yielded unchanged starting material (0.184 g.) and chloroform eluted a further 0.106 g. Continuing the chloroform elution gave a colourless syrup (0.491 g.) which crystallised under light petroleum (b. p. 60—80°). This was drained on tile, kept for several days, and recrystallised several times from light petroleum. Methyl 4 : 6-O-benzylidene-3-bromo-3-deoxy- $\alpha$ -D-altroside (0.21 g., 15.7%) resulting had m. p. 123—124°,  $[\alpha]_D^{25} + 120^\circ$  (c, 0.5 in  $\text{CHCl}_3$ ) (Found: C, 48.9; H, 5.0.  $\text{C}_{14}\text{H}_{17}\text{O}_5\text{Br}$  requires C, 48.7; H, 5.0%).

(c) *Magnesium chloride.* (i) On treatment in ether as described above, but after 8 hours' heating under reflux with an excess of magnesium chloride, 95% of the starting material was recovered. No other product was isolated and no alkalinity was detected on addition of water to the reaction mixture. (ii) A solution of the anhydromannoside (1.04 g.) in tetrahydropyran (25 c.c.) was heated with anhydrous magnesium chloride (2 g.) in a sealed tube at 110° for 8 hr., then at 140° for 4 hr.; it darkened considerably. It was treated as described above, and the dark brown syrup obtained chromatographed on alumina. A fraction containing chlorine was ultimately obtained by elution with chloroform; this was a brown syrup (0.070 g.).

*Attempted Methylation of Methyl 4 : 6-O-Benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside.*—The altroside (0.514 g.) was heated under reflux for 18 hr. with silver oxide (1 g.) and methyl iodide (5 c.c.). The product (0.330 g., 95%), isolated in the usual way, was methyl 2 : 3-anhydro-4 : 6-O-benzylidene- $\alpha$ -D-mannoside, m. p. and mixed m. p. 146—147°.

When the altroside (87 mg.) in chloroform (1 c.c.) was treated with a solution from sodium (60 mg.) and absolute methanol (3 c.c.) for 20 hr. at room temperature, the same product was isolated (56 mg., 96%).

*Reduction of Methyl 4 : 6-O-Benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside.*—The altroside (0.525 g.) in ethanol (20 c.c.) and water (7 c.c.) was boiled with barium carbonate (2 g.) and Raney nickel (*ca.* 15 g.) in ethanol (10 c.c.) with stirring for 2 hr. The mixture was then filtered and evaporated to a colourless syrup which was dissolved in water (10 c.c.) and washed several times with chloroform. Evaporation of the aqueous solution yielded a colourless syrup which was dissolved in ethyl acetate-ethanol, filtered from barium iodide, and concentrated to small volume. Colourless cubic crystals of methyl 3-deoxy- $\alpha$ -D-mannoside separated when the solution was kept at 0° and, recrystallised from acetone, had  $[\alpha]_D^{25} + 134.6^\circ$  (*c.* 2 in MeOH), *m. p.* 123.5—124° (Found: C, 47.5; H, 7.92. Calc. for  $C_7H_{14}O_5$ : C, 47.2; H, 7.92%). Bollinger and Prins (*loc. cit.*) describe this compound as an amorphous solid, showing  $[\alpha]_D^{15} + 108.9^\circ \pm 2^\circ$  (*c.* 2 in MeOH).

The crystalline product was not oxidised by lead tetra-acetate in acetic acid under the conditions described by Hockett and McClenahan (*J. Amer. Chem. Soc.*, 1939, **61**, 1667).

*Reduction of Methyl 4 : 6-O-Benzylidene-3-bromo-3-deoxy- $\alpha$ -D-altroside.*—The altroside (72 mg.) was heated under reflux for 2 hr. with barium carbonate (0.5 g.) and Raney nickel (*ca.* 4 g.) in ethanol (9 c.c.) and water (2 c.c.). Then the cooled solution was filtered and the solids were washed with hot water. The combined filtrates were evaporated to *ca.* 10 c.c., and the aqueous solution was washed several times with chloroform and then evaporated to dryness. The residual colourless viscous syrup was extracted with hot acetone and filtered. When the acetone extract was concentrated and treated with ether, methyl 3-deoxy- $\alpha$ -D-mannoside separated (30 mg., 80%); it had *m. p.* 123—124° (from acetone-ether) alone or in admixture with the compound described above, and  $[\alpha]_D^{25} + 129.6^\circ$  (*c.* 1 in MeOH) (Found: C, 47.3; H, 8.2%).

*General Procedure for the Reaction of Various Anhydro-sugars and Anhydrohexitols with 0.5N-Hydrochloric Acid Saturated with Magnesium Chloride.*—The anhydride (0.05 g.) was added to 0.5N-hydrochloric acid saturated with magnesium chloride (3 c.c.), and the mixture kept at room temperature for 15 min. and then titrated with 0.2N-sodium hydroxide. The results obtained are recorded on p. 498.

*Methyl 3-Chloro-3-deoxy-4 : 6-di-O-methyl- $\alpha$ -D-glucoside.*—To methyl 2 : 3-anhydro-4 : 6-di-O-methyl- $\alpha$ -D-alloside (1 g.) was added 0.5N-hydrochloric acid saturated with potassium chloride (20 c.c.), and the mixture kept overnight at 27°, neutralised with sodium hydroxide, and extracted with ether (5  $\times$  100 c.c.). The extract was dried ( $MgSO_4$ ), filtered and evaporated. The resulting syrup distilled at 130°/0.02 mm. and had  $n_D^{25}$  1.4729 and  $[\alpha]_D^{25} + 147^\circ$  (*c.* 0.8 in  $CHCl_3$ ), then crystallised. Recrystallised from ether-light petroleum, methyl 3-chloro-3-deoxy-4 : 6-di-O-methyl- $\alpha$ -D-glucoside had *m. p.* 77—78°  $[\alpha]_D^{25} + 160^\circ$  (*c.* 1.1 in  $CHCl_3$ ) (Found: C, 45.3; H, 7.2; Cl, 15.1.  $C_9H_{17}O_5Cl$  requires C, 44.9; H, 7.1; Cl, 14.8%).

*Hydrolysis of Methyl 3-Chloro-3-deoxy-4 : 6-di-O-methyl- $\alpha$ -D-glucoside and Treatment of the Product with Sodium Metaperiodate.*—The chloroglucoside (0.093 g.) was heated with 2N-hydrochloric acid (10 c.c.) at 100° until the rotation was constant  $\{[\alpha]_D^{25} + 164^\circ$  (allowing for hydrolysis of methyl glucoside group), after 20 hr.}, then cooled and made up to 25 c.c. Aliquot parts were added to 5 c.c. of 0.184N-sodium metaperiodate containing a slight excess of sodium hydrogen carbonate. After  $1\frac{1}{2}$  hr., 0.92 mol. of periodate was consumed.

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, EDGBASTON, BIRMINGHAM 15.  
THE DEPARTMENT OF SUGAR CHEMISTRY AND TECHNOLOGY,  
THE IMPERIAL COLLEGE OF TROPICAL AGRICULTURE,  
TRINIDAD.

[Received, August 15th, 1955.]