334. *The Behaviour of Anhydromethylhexosides towards Alkaline Reagents. Preparation of Derivatives of 3-Amino-glucose and 2-Amino-altrose.*

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Methods have been developed for the synthesis of amino-sugars by the action of ammonia on anhydromethylhexosides. *Tetra-acetyl 3-amino-α-methylglucoside* has been obtained by appropriate reactions from 3-*p*-toluenesulphonyl triacetyl α-methylglucoside, from 4 : 6-benzylidene-2 : 3-anhydro-α-methylalloside and from 3 : 4-anhydro-α-methylalloside. In the β-series, 3 : 4-anhydro-β-methylalloside gives *tetra-acetyl 3-amino-β-methylglucoside*, which is converted into the α-isomeride by methyl-alcoholic hydrogen chloride. The preparation of the α- and the β-form of *trimethyl 3-acetamido-methylglucoside* is described and a number of other derivatives of 3-amino-glucose are characterised.

In addition, it is shown that a mixture of 4 : 6-*benzylidene 2-amino-α-methylaltroside diacetate* and 4 : 6-*benzylidene 3-amino-α-methylglucoside diacetate* in the proportion 10 : 1 is obtained from 4 : 6-benzylidene 2 : 3-anhydro-α-methylalloside.

Further examples are given of the mode of scission by alkali of the anhydro-ring in 2 : 3-anhydro-β-methylalloside and the following crystalline derivatives are described: 4 : 6-*benzylidene 3-methyl β-methylglucoside*, 4 : 6-*benzylidene 2-methyl β-methylaltroside*, 4 : 6-*dimethyl β-methylaltroside*.

THE interest attaching to glucosamine and other amino-sugars of biological importance has led us to investigate the possibilities of synthesis in this group. The ease of scission by alkali of the oxide ring in anhydro-sugars indicates the suitability of these compounds as intermediates in syntheses of the type in question and it has in fact been found possible to introduce the amino-group into a sugar molecule by the action of ammonia on such anhydrides.

The preparation of 3-amino-altrose by the action of ammonia on a derivative of 2-*p*-toluenesulphonyl glucose (Bodycote, Haworth, and Hirst, J., 1934, 151) undoubtedly occurs by the intermediate formation of a 2 : 3-anhydromannose (cf. Lake and Peat, this vol., p. 1417) and thus provides an example of the type of reaction here envisaged. Freudenberg, Burkhart, and Braun (*Ber.*, 1926, **59**, 714) were able to prepare 3-amino-glucose diacetone by the action of ammonia on the corresponding 3-*p*-toluenesulphonyl

derivative. No possibility exists in this preparation of the formation of anhydride linkages and for that reason the interchange is not attended by a Walden inversion and the amino-sugar most probably retains the glucose configuration. In a similar manner we have prepared *tetra-acetyl 3-amino-α-methylglucoside* (IV) by the action of ammonia on triacetyl 3-*p*-toluenesulphonyl α-methylglucoside (V) (cf. Peat and Wiggins, this vol., p. 1088), followed by acetylation of the product. The possibility of anhydro-ring formation under the influence of the alkaline reagent is not excluded in this case and the product may have been a derivative of glucose, altrose, or gulose. That it was indeed a derivative of glucose became evident when it was also obtained by the action of ammonia on derivatives of both 2 : 3- and 3 : 4-anhydromethylallosides.

It was shown by Peat and Wiggins (*loc. cit.*) that 3-*p*-toluenesulphonyl methylglucoside yields, when treated with alkali, a mixture of 2 : 3-anhydromethylalloside (60%), 3 : 4-anhydromethylalloside (25%), and 3 : 6-anhydromethylglucoside (15%). The first of these components is separated as the benzylidene derivative, and the second as a crystalline dimethyl derivative. The separation of the 3 : 4-anhydro- and 3 : 6-anhydro-substances is incomplete and, as the 3 : 6-anhydro-ring is stable to ammonia, the mixture of 3 : 4-anhydromethylalloside (60%), and 3 : 6-anhydromethylglucoside (40%) was used as a source of the former substance in the experiments described below.

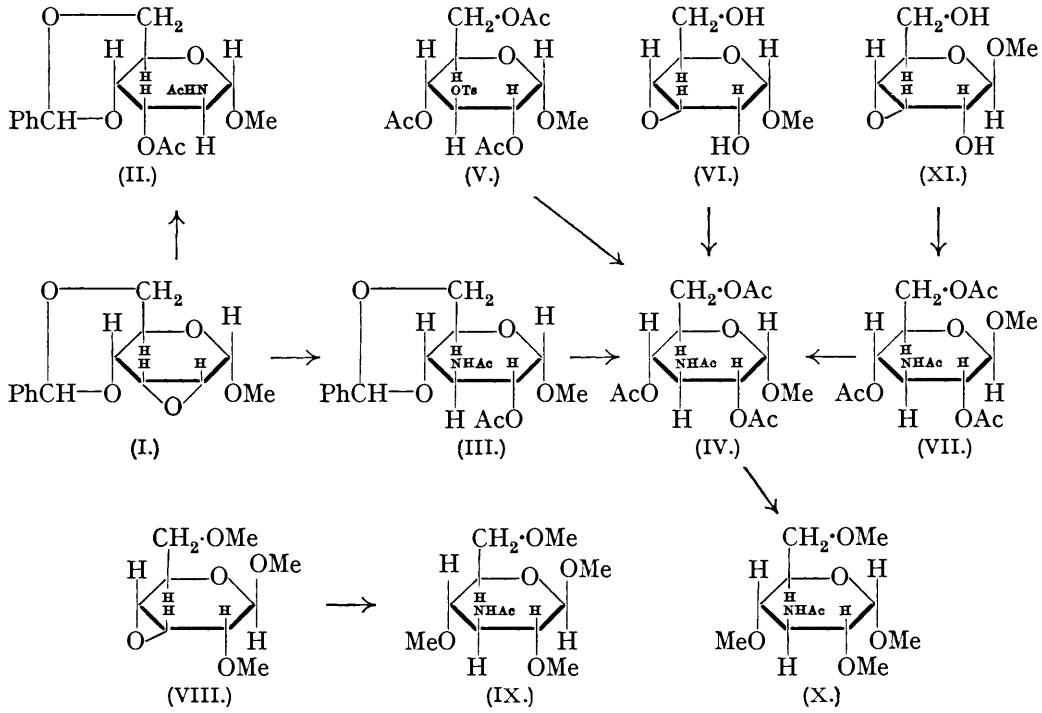
The derivatives of two amino-sugars are obtained when 4 : 6-benzylidene 2 : 3-anhydro-α-methylalloside (I) is heated under pressure with methyl-alcoholic ammonia. These products, which are conveniently isolated as the crystalline acetates, are formed in the proportion 1 : 10. Since the hydrolysis of the same compound (I) with sodium methoxide results in the isolation of a derivative of altrose in 87% yield (Robertson and Griffith, J., 1935, 1197), it is reasonable to assume that, of the two acetates obtained here, that which preponderates is 4 : 6-*benzylidene 2-amino-α-methylaltroside diacetate* (II), the other constituent of the mixture being 4 : 6-*benzylidene 3-amino-α-methylglucoside diacetate* (III)—a conclusion that follows from considerations of the mode of scission of the ethylene-oxide ring in sugars (Peat and Wiggins, *loc. cit.*). Removal of the benzylidene group from the glucoside (III) was effected by treatment with 0·5% methyl-alcoholic hydrogen chloride. Acetylation of the product gave tetra-acetyl 3-amino-α-methylglucoside (IV) identical with that prepared directly from the *p*-toluenesulphonate (V).

The hydrolysis by means of ammonia of a 3 : 4-anhydromethylalloside should lead, in an analogous manner, to the formation of derivatives of 3-amino-glucose and 4-amino-gulose. In the earlier paper it is shown that, when sodium methoxide is used as the hydrolytic agent, derivatives of 3-methyl glucose (*ca.* 70%) and 4-methyl gulose (*ca.* 30%) are produced together. We have been unable to isolate the amino-gulose constituent in the present case, but ample evidence has been obtained of the formation of amino-glucose. The mixture of 3 : 4-anhydro-α-methylalloside (VI) and 3 : 6-anhydro-α-methyl-glucoside prepared as described yielded, on treatment with ammonia, crystalline *3-amino-α-methylglucoside*. The last-named substance was smoothly converted into the tetra-acetate (IV) by acetylation. It was clear from the yield that the 3-amino-methylglucoside must have been derived from the 3 : 4-anhydromethylalloside and not from the very small amount of 2 : 3-anhydromethylalloside likely to be present in the mixture of anhydro-methylglycosides.

A study of the action of ammonia on 3 : 4-anhydro-β-methylalloside (XI) revealed no essential difference in the mode of scission of the anhydro-ring in the α- and the β-series. From (XI) was prepared 3-amino-β-methylglucoside and its hydrochloride. Both of these substances are described by Freudenberg, Burkhart, and Braun (*loc. cit.*). Acetylation of 3-amino-β-methylglucoside gave tetra-acetyl 3-amino-β-methylglucoside (VII), the constitution of which as a derivative of glucose was established by its conversion, when treated with 2% methyl-alcoholic hydrogen chloride, into the α-isomeride (IV) (cf. Cutler, Haworth, and Peat, J., 1937, 1979).

3-Amino-glucose was isolated as a syrup when the tetra-acetate (IV) was hydrolysed with mineral acid, and oxidation of the free sugar with mercuric oxide yielded a hygroscopic solid, the constants of which were in fair agreement with those ascribed by Freudenberg, Burkhart, and Braun to 3-amino-gluconic acid.

When the crystalline dimethyl 3 : 4-anhydro-β-methylalloside (VIII) is submitted to the action of ammonia, and the product acetylated, there is obtained the diacetate of a dimethyl methylhexoside which, for reasons similar to those given above, is regarded as 4-*acetyl* 2 : 6-*dimethyl* 3-*acetamido*-β-*methylglucoside*. By treatment of this product with methyl sulphate and sodium hydroxide solution, the *O*-acetyl is replaced by a methyl group and *trimethyl* 3-*acetamido*-β-*methylglucoside* (IX) results. The α-isomeride (X) of this compound is prepared by the simultaneous deacetylation and methylation of the tetra-acetate (IV).



We have been able to show by further examples that the hydrolytic opening of an anhydro-ring in a sugar takes place in two directions and that, in favourable circumstances, derivatives of two configurationally isomeric sugars may be isolated as products of such hydrolysis. The formation described above of a mixture of derivatives of 3-amino-methylglucoside and 2-amino-methylaltroside from a 2 : 3-anhydromethylalloside is a case in point. In addition, it has been found that treatment of dimethyl 2 : 3-anhydro-β-methylalloside with sodium methoxide produces a mixture of crystalline 3 : 4 : 6-trimethyl β-methylglucoside (5%) and a syrup (66%) which is, by analogy, 2 : 4 : 6-*trimethyl* β-*methylaltroside*. The glucoside was identical (by mixed melting point determination) with that prepared by Haworth, Hirst, and Panizzon (J., 1934, 154). Acid hydrolysis of the altroside gave 2 : 4 : 6-trimethyl altrose ($[\alpha]_D$ + 38·2°), which also was a syrup. Robertson and Dunlop (this vol., p. 476) give $[\alpha]_D$ + 79·3° for this compound prepared from the α-methylaltroside. It is to be observed, however, that these authors did not separate any glucose in their experiments.

A better example was found in the hydrolysis with sodium methoxide of 4 : 6-benzylidene 2 : 3-anhydro-β-methylalloside, for, in this case, the products were both crystalline. They were 4 : 6-*benzylidene* 3-*methyl* β-*methylglucoside* (12%) and 4 : 6-*benzylidene* 2-*methyl* β-*methylaltroside* (72%). That the first-named compound was actually a glucose derivative was shown by its methylation to form a product identical in melting point and rotation with the 4 : 6-benzylidene 2 : 3-dimethyl β-methylglucoside prepared from glucose by Freudenberg, Toepffer, and Anderson (*Ber.*, 1928, **61**, 1758).

It has already been indicated that in the hydrolysis of 2 : 3-anhydromethylalloside and its derivatives, the chief product has the altrose configuration, the amount of glucose formed at the same time rarely exceeding 10% of the mixture. This disproportion accounts for the failure in some cases to isolate the glucose constituent. Thus in the hydrolysis of dimethyl 2 : 3-anhydro-β-methylalloside with aqueous potassium hydroxide only the altrose derivative was isolated.* This was 4 : 6-*dimethyl β-methylaltroside*, which, unlike the α-isomeride prepared by Robertson and Dunlop (*loc. cit.*), was crystalline (m. p. 118°; $[\alpha]_D^{19°}$ − 49·3°) and non-hygroscopic. It was clearly the altroside and not the glucoside which had been isolated, since 4 : 6-dimethyl β-methylglucoside has m. p. 50—52°; $[\alpha]_D^{18°}$ − 28·8° (Bell and Synge, J., 1937, 1711). It was not found possible to prepare a crystalline 4 : 6-dimethyl altrose by acid hydrolysis of the β-methylaltroside.

Experimental.

Action of Ammonia on 4 : 6-*Benzylidene* 2 : 3-*Anhydro-α-methylalloside* (I).—The α-methylalloside (1·98 g.), prepared by the method of Peat and Wiggins (*loc. cit.*), was dissolved in methyl alcohol (60 c.c.) saturated with dry ammonia at 0°, and heated in a sealed tube at 150° for 35 hours. The solution was then evaporated, and the residue freed from ammonia by heating at 80° in a vacuum for several hours. The product (2 g.) separated as a gel from either methyl alcohol or chloroform–petrol. It had m. p. 162—166° and $[\alpha]_D^{20°}$ + 119° in chloroform (*c*, 0·75).

In a second experiment, the α-methylalloside (3·3 g.) was heated at 140° with methyl-alcoholic ammonia for 3 days. The product was acetylated by treatment with acetic anhydride (3·4 c.c.) and pyridine (30 c.c.) at room temperature for 48 hours and the solution was then diluted with chloroform and washed successively with 5% sulphuric acid, sodium bicarbonate solution, and water. Evaporation of the dried chloroform solution left a crystalline acetate (3·2 g.), which was separated by crystallisation from methyl alcohol and from ether into two fractions: Fraction A (0·27 g.), m. p. 270°, $[\alpha]_D^{18°}$ + 44·6° in chloroform (*c*, 1·01); and fraction B (2·5 g.), m. p. 184°, $[\alpha]_D^{18°}$ + 52·5° in chloroform (*c*, 1·45). For reasons given above, substance (A) is recognised as 2-*acetyl* 4 : 6-*benzylidene* 3-*acetamido-α-methylglucoside* (III) (Found: C, 59·3; H, 6·4; N, 4·2. $C_{18}H_{23}O_7N$ requires C, 59·2; H, 6·3; N, 3·9%), and fraction B as 3-*acetyl* 4 : 6-*benzylidene* 2-*acetamido-α-methylaltroside* (II) (Found: N, 3·9%).

Triacetyl 3-*Acetamido-α-methylglucoside*.—The α-methylglucoside (A) (0·125 g.) was heated at 55° with 0·5% methyl-alcoholic hydrogen chloride until the rotation became constant at $[\alpha]_D$ + 106°. The syrup obtained after neutralisation and evaporation to dryness was boiled for 5 minutes with acetic anhydride (2 c.c.) and sodium acetate (0·5 g.). The product, isolated in the usual way, was *triacetyl* 3-*acetamido-α-methylglucoside* (IV). It had m. p. 178°, $[\alpha]_D^{20°}$ + 101·9° in chloroform (*c*, 1·07), and the yield (after recrystallisation from acetone) was 0·05 g. (Found: C, 49·6; H, 6·5; N, 3·9. $C_{15}H_{23}O_9N$ requires C, 49·8; H, 6·4; N, 3·9%).

The Action of Ammonia on 3 : 4-*Anhydro-α-methylalloside* (VI).—The alkaline hydrolysis product of 3-*p*-toluenesulphonyl triacetyl α-methylglucoside has been shown by Peat and Wiggins (*loc. cit.*) to consist of a mixture of three anhydro-α-methylhexosides. The 2 : 3-anhydromethylalloside was removed from this mixture (5·3 g.) as the benzylidene derivative and the residue (2·9 g.), consisting of 3 : 4-anhydro-α-methylalloside (60%) and 3 : 6-anhydro-α-methylglucoside (40%), was heated with methyl-alcoholic ammonia at 150° for 35 hours. The product of this treatment was separated by solution in methyl alcohol into a crystalline fraction (A) (0·8 g.) and a syrupy fraction (B) (1·9 g.). The substance (A) was 3-*amino-α-methylglucoside* and, after recrystallisation from methyl alcohol, showed m. p. 167—168° and $[\alpha]_D^{18°}$ + 144·4° in water (*c*, 0·85) (Found: C, 43·8; H, 7·7; N, 8·0. $C_7H_{15}O_5N$ requires C, 43·5; H, 7·7; N, 7·3%). On acetylation with acetic anhydride and sodium acetate, this substance was converted into tetra-acetyl 3-amino-α-methylglucoside (m. p. 178°; $[\alpha]_D^{19°}$ + 101° in chloroform) identical with that prepared from the 2 : 3-anhydro-α-methylalloside (see above). The syrup (B) consisted principally of the 3 : 6-anhydromethylglucoside, which is not affected

* *Note added in proof* (October 29th). This statement now needs emendation. In the interval, the glucose constituent of the mixture has been isolated in crystalline form from the mother-liquors after recrystallisation of the 4 : 6-dimethyl β-methylaltroside. The product (10 mg. from 0·23 g. of trimethyl 2 : 3-anhydro-β-methylalloside) has m. p. 51—52° and $[\alpha]_D^{20°}$ − 27·8° in chloroform (*c*, 0·94) (Found: OMe, 41·3%). It gives no depression of m. p. in admixture with an authentic specimen of 4 : 6-dimethyl β-methylglucoside (kindly provided by Dr. D. J. Bell).

by ammonia. It contained also a little of the 3-amino-α-methylglucoside, for on acetylation of the syrup the tetra-acetate (0·25 g.) was obtained.

The Action of Ammonia on 3 : 4-*Anhydro*-β-*methylalloside* (XI).—By the hydrolysis of the β-isomeride of 3-*p*-toluenesulphonyl triacetyl methylglucoside (11 g.), the mixture of anhydro-β-methylhexosides was obtained and from the latter (2·85 g.), the 2 : 3-anhydro-β-methylalloside was removed as the benzylidene derivative. The remaining syrup (2 g.) was treated with ammonia as described for the α-isomeride. In this way 3-amino-β-methylglucoside (0·35 g.) was obtained. After recrystallisation from methyl alcohol, this substance showed m. p. 206° and $[\alpha]_D^{21°}$ — 47·4° in water (*c*, 0·81) (Found: C, 43·7; H, 7·9%). A small amount (25 mg.) was converted into the hydrochloride by treatment in the cold for 1 hour with 5% methyl-alcoholic hydrogen chloride and neutralisation with lead carbonate. The hydrochloride (15 mg.) had m. p. 185° (decomp. at 206°) and $[\alpha]_D^{20°}$ — 35° (approx.) in water (Found: C, 36·7; H, 7·2; N, 7·3; Cl, 15·9. Calc. for $C_7H_{15}O_5N$,HCl: C, 36·7; H, 7·0; N, 6·1; Cl, 15·5%). Freudenberg, Burkhart, and Braun (*loc. cit.*) record m. p. 206° and $[\alpha]_D$ — 46·6° (in water) for this compound, prepared from diacetone glucose.

3-Amino-β-methylglucoside (0·2 g.) on acetylation in the usual way with acetic anhydride and sodium acetate gave *triacetyl* 3-*acetamido*-β-*methylglucoside* (VII) (0·19 g.), which, after recrystallisation from chloroform–petrol, had m. p. 160° and $[\alpha]_D^{18°}$ — 21·4° in chloroform (*c*, 1·124) (Found: C, 50·3; H, 6·6; N, 4·1%).

Conversion into the α-*isomeride.* Tetra-acetyl 3-amino-β-methylglucoside (0·13 g.) was boiled with 2% methyl-alcoholic hydrogen chloride (10 c.c.) for 11 hours, during which the rotation changed from $[\alpha]_D$ — 17° to + 61·5°. The solution was neutralised with silver carbonate and filtered, and the solvent evaporated. The residue was acetylated with acetic anhydride and sodium acetate. The product (0·085 g.), after recrystallisation, had m. p. 177° and $[\alpha]_D^{20°}$ + 101° in chloroform. It showed no depression of m. p. in admixture with tetra-acetyl 3-amino-α-methylglucoside.

Action of Ammonia on 3-p-*Toluenesulphonyl* α-*Methylglucoside Triacetate* (V).—The substance (30 g.) was heated in sealed tubes at 150° for 30 hours with methyl alcohol (150 c.c.) saturated with ammonia (at 0°). Thereafter, the solution was evaporated, and the residue heated at 95° in a vacuum for several hours. Solution of the syrup in alcohol and addition of ether precipitated ammonium *p*-toluenesulphonate. The filtrate therefrom was evaporated, and the syrupy residue acetylated by treatment with acetic anhydride (200 c.c.) and sodium acetate (40 g.). The product (5·5 g.), after three recrystallisations from acetone, showed $[\alpha]_D^{19°}$ + 101·7° in chloroform and m. p. 178·5° (alone or in admixture with tetra-acetyl 3-amino-α-methylglucoside).

Hydrolysis of Tetra-acetyl 3-*Amino*-α-*methylglucoside.*—The glucoside (4·9 g.) was heated on a water-bath with 6% hydrochloric acid for 34 hours, during which time $[\alpha]_D$ changed from + 111° to + 38° (constant value). Neutralisation of the solution with silver carbonate and evaporation to dryness yielded 3-amino-glucose as a syrup (2·1 g.), which showed $[\alpha]_D^{20°}$ + 18·4° in water (*c*, 1·25). 3-Amino-glucose was oxidised by heating in water with yellow mercuric oxide. 3-Amino-gluconic acid was so obtained as a hygroscopic solid which could not be crystallised: $[\alpha]_D^{21°}$ + 12·9° in water (*c*, 1·7). Freudenberg, Burkhart, and Braun (*loc. cit.*) give m. p. 168° (decomp.) and $[\alpha]_{5780}$ + 13° for this compound.

Methylation of Tetra-acetyl 3-*Amino*-α-*methylglucoside.*—The substance (4 g.) was dissolved in water (200 c.c.), the solution mixed with carbon tetrachloride (200 c.c.), and the mixture treated (with vigorous stirring) with methyl sulphate (50 c.c.) and 30% sodium hydroxide solution (240 c.c.) at 50° (cf. Holden and West, *J. Amer. Chem. Soc.*, 1934, **56**, 930). A product (0·5 g.) was obtained which, after recrystallisation from ethyl acetate, had m. p. 156° (decomp.) and $[\alpha]_D^{17°}$ + 131·1° in chloroform (*c*, 1·06). This substance is 2 : 4 : 6-*trimethyl* 3-*acetamido*-α-*methylglucoside* (X) (Found: C, 51·6; H, 8·3; N, 5·05; OMe, 44·0. $C_{12}H_{23}O_6N$ requires C, 51·9; H, 8·3; N, 5·05; OMe, 44·7%).

The Action of Ammonia on Dimethyl 3 : 4-*Anhydro*-β-*methylalloside* (VIII).—[For the preparation of this crystalline derivative, see Peat and Wiggins (*loc. cit.*).] The substance (1 g.) was heated at 130° for 30 hours with methyl-alcoholic ammonia (50 c.c.). The syrupy product distilled at 120—125°(bath temp.)/0·02 mm. without decomposition. The distillate (1 g., $n_D^{18°}$ 1·4781) was acetylated with acetic anhydride and sodium acetate and the product (0·9 g.) was separated by crystallisation from ethyl acetate–petrol into a crystalline fraction (0·65 g.) and a syrup (0·2 g.). The crystalline substance is 4-*acetyl* 2 : 6-*dimethyl* 3-*acetamido*-β-*methylglucoside*, m. p. 142°, $[\alpha]_D^{21°}$ — 50·9° in chloroform (*c*, 1·19) (Found: C, 51·0; H, 7·6; OMe, 20·1. $C_{13}H_{23}O_7N$ requires C, 51·1; H, 7·5; OMe, 20·4%).

This acetate (0·45 g.) was treated with methyl sulphate and sodium hydroxide solution in the presence of carbon tetrachloride as described previously and *trimethyl* 3-*acetamido*-β-*methylglucoside* (IX) (0·2 g.) was produced. The product, after recrystallisation from ethyl acetate–petrol, had m. p. 134—135° and $[\alpha]_D^{21°}$ — 82·9° in chloroform (*c*, 1·17) (Found : C, 51·4; H, 8·4; N, 4·9; OMe, 44·8%).

Action of Sodium Methoxide Solution on Dimethyl 2 : 3-*Anhydro*-β-*methylalloside*.—The β-methylalloside (m. p. 50—51°; 0·43 g.) was boiled for 30 hours, with methyl alcohol (10 c.c.) containing 5% of sodium methoxide. The product, isolated as described in the previous paper, distilled at 110—115°(bath temp.)/0·025 mm. and had $n_D^{21°}$ 1·4565. Yield, 0·41 g. On keeping, partial crystallisation occurred and it was possible, by spreading on a porous tile, to separate the crystalline fraction from the syrup. The crystalline fraction was 3 : 4 : 6-trimethyl β-methylglucoside and showed, after recrystallisation from ether–petrol, m. p. 51—52° (alone or in admixture with an authentic specimen) and $[\alpha]_D^{19°}$ — 20·9° in chloroform (*c*, 1·34) (Found : OMe, 52·1. Calc. for $C_{10}H_{20}O_6$: OMe, 52·5%). Yield, 0·02 g., *i.e.*, 5% of the mixture.

The syrupy fraction, extracted from the tile, was for the greater part 2 : 4 : 6-trimethyl β-methylaltroside. It distilled at 105°(bath temp.)/0·02 mm. and showed $n_D^{22°}$ 1·4545; $[\alpha]_D^{21°}$ — 18·1° in chloroform (*c*, 1·12) (Found : OMe, 52·3%). Yield, 0·23 g., *i.e.*, 66% of the mixture. The β-methylaltroside (0·22 g.) was hydrolysed by heating at 95° with 5% hydrochloric acid for 13 hours, during which time $[\alpha]_D$ changed to + 76·2°. The product, 2 : 4 : 6-trimethyl altrose, was obtained as a syrup (0·18 g.) of $[\alpha]_D^{18°}$ + 38·2° in chloroform (*c*, 1·7) (Found : OMe, 41·4. Calc. for $C_9H_{18}O_6$: OMe, 41·9%). Robertson and Dunlop (*loc. cit.*) give $[\alpha]_D^{15°}$ + 79·3° (in chloroform) for this compound.

Action of Aqueous Potassium Hydroxide on Dimethyl 2 : 3-*Anhydro*-β-*methylalloside*.—The substance (0·23 g.) was heated on a boiling water-bath with 5% potassium hydroxide solution for 20 hours, during which $[\alpha]_D$ changed from + 43·2° to — 17·3°. Thereafter the cooled solution was saturated with potassium bicarbonate and exhaustively extracted with chloroform. The dried chloroform extract yielded a syrup (0·21 g.), which crystallised after distillation at 130—135°(bath temp.)/0·025 mm. The product, 4 : 6-*dimethyl* β-*methylaltroside*, separated from ether in large prisms, m. p. 118°, $[\alpha]_D^{19°}$ — 49·3° in chloroform (*c*, 1·54) (Found : OMe, 41·0. $C_9H_{18}O_6$ requires OMe, 41·9%). Complete hydrolysis of the altroside was effected by heating on a boiling water-bath with 2% hydrochloric acid for 4½ hours ($[\alpha]_D$ + 56·5°, calculated on a dimethyl hexose) and 4 : 6-dimethyl altrose (0·05 g.) was isolated as a reducing syrup (Found : OMe, 29·4. Calc. for $C_8H_{16}O_6$: OMe, 29·8%). The amount of material available was too small for further purification to be attempted. Robertson and Griffith (*loc. cit.*) record m. p. 158—160° and $[\alpha]_D^{15°}$ + 102·9° ⟶ + 64·9° (constant value in water) for this compound.

Action of Sodium Methoxide Solution on 4 : 6-*Benzylidene* 2 : 3-*Anhydro*-β-*methylalloside*.—The material (2 g.) was boiled with 5% sodium methoxide solution (70 c.c.) for 24 hours. The product (2·3 g.), extracted in the usual way, was crystalline and was separated by crystallisation from a minimum quantity of methyl alcohol into 4 : 6-*benzylidene* 3-*methyl*-β-*methylglucoside* (m. p. 166°) and 4 : 6-*benzylidene* 2-*methyl* β-*methylaltroside* (m. p. 127—129°). The β-methylglucoside, recrystallised from ethyl alcohol, showed $[\alpha]_D^{17°}$ — 46·0° in chloroform (*c*, 1·265) (Found : OMe, 20·6. $C_{15}H_{20}O_6$ requires OMe, 21·0%). Yield, 0·3 g., *i.e.*, 12% of the crude mixture. The β-methylaltroside separated from chloroform–light petroleum in small prisms, $[\alpha]_D^{18°}$ — 48·0° in chloroform (*c*, 1·86); yield, 1·7 g., *i.e.*, 72% of the mixture (Found : OMe, 20·9%).

4 : 6-Benzylidene 3-methyl β-methylglucoside (0·1 g.) was methylated by three treatments with Purdie's reagents and gave 4 : 6-benzylidene 2 : 3-dimethyl β-methyglucoside (0·08 g.) of m. p. 134° and $[\alpha]_D^{16°}$ — 60·2° in chloroform (*c*, 0·856) (Found : OMe, 29·7. Calc. for $C_{16}H_{22}O_6$: OMe, 30·1%). Freudenberg, Toepffer, and Anderson (*loc. cit.*) record m. p. 134° and $[\alpha]_D^{23°}$ — 61·0° (in alcohol) for this compound.

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