130. *The Action of Alkaline Reagents on 2 : 3-1 : 6- and 3 : 4-1 : 6-Dianhydro β-Talose. A Constitutional Synthesis of Chondrosamine and Other Amino-sugar Derivatives.*

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The action of ammonia and of sodium methoxide on 2 : 3-1 : 6- (I) and 3 : 4-1 : 6-dianhydro β-talose (II) has been investigated. With ammonia (I) gave 2-*amino* 1 : 6-*anhydro β-galactose*, hydrolysis with hydrochloric acid of the 1 : 6-anhydro ring of which afforded 2-amino galactose hydrochloride (identical with naturally occurring chondrosamine hydrochloride) and 3-amino 1 : 6-anhydro β-idose. The latter was also obtained by the action of ammonia from the isomeric dianhydride (II) together with 4-amino 1 : 6-anhydro β-mannose isolated as its *hydrochloride*. Both dianhydrides underwent ring scission on sodium methoxide treatment, (I) giving 2-methyl 1 : 6-anhydro β-galactose and (II) giving 4-methyl 1 : 6-anhydro β-mannose. No crystalline derivative of 3-methyl 1 : 6-anhydro β-idose, which theoretically should also have been formed, could be isolated.

A brief outline of a constitutional synthesis of chondrosamine from 2 : 3-1 : 6-dianhydro β-talose has been given (James *et al.*, *Nature*, 1945, **156**, 308). In the present paper this synthesis is described in detail and the work has been extended to include a study of the action of sodium methoxide on 1 : 6-anhydro talose derivatives.

It is now well established in the sugar series that scission of an anhydro ring of the ethylene oxide type, in which the ring does not engage a primary alcoholic group, takes place on both sides of the oxygen bridge and in each case is accompanied by Walden inversion giving rise to two isomeric sugar derivatives (Peat, *Ann. Reports*, 1939, **36**, 288). It has usually been observed that the amount of one isomer largely predominates over that of the other. Thus ring scission of 4 : 6-benzylidene 2 : 3-anhydro α-methylalloside gives 2-methyl 4 : 6-benzylidene α-methylaltroside and 3-methyl 4 : 6-benzylidene α-methylglucoside in the ratio of 10 : 1 (Peat and Wiggins, *J.*, 1938, 1088). Frequently the secondary component is formed in such minute amounts as to make its isolation difficult and indeed only possible when it crystallises with particular ease or when its solubility properties differ widely from those of the primary product. An interesting example is the ring scission of 4 : 6-benzylidene 2 : 3-anhydro β-methyltaloside with alkaline reagents (Wiggins, *J.*, 1944, 522). With sodium methoxide there were obtained 3-methyl 4 : 6-benzylidene β-methylidoside and 2-methyl 4 : 6-benzylidene β-methylgalactoside. The latter was obtained with difficulty and only in small yields but the two products sufficed to determine the constitution of the anhydro compound. When this was treated with ammonia only 3-amino 4 : 6-benzylidene β-methyltaloside (63% yield) could be isolated, though a very small amount of the 2-amino galactose derivative may also have been formed.

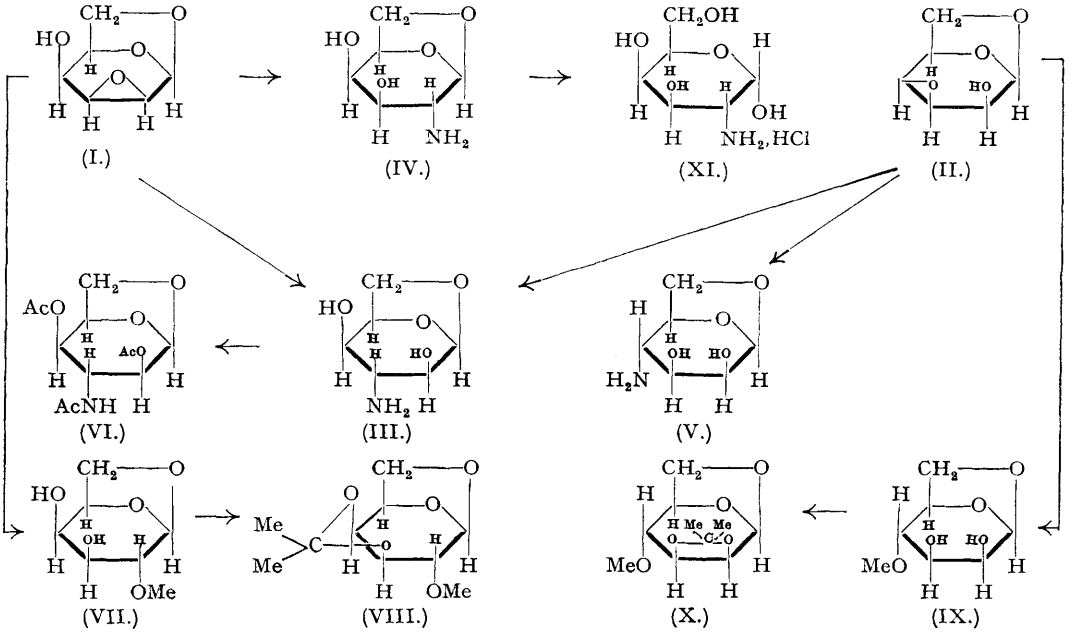
In the present work we have studied the action of both ammonia and sodium methoxide on a closely related compound in which the β-methyl glycosidic group was replaced by a β-1 : 6-anhydro ring. Here, in contrast, the 2-amino and 2-methyl derivatives predominated. We have also been able to compare the reaction of the two alkaline reagents on an isomeric dianhydride of talose (II) in which the ethylene oxide ring engages the 3 and 4 positions.

2 : 3-1 : 6-Dianhydro β-talose (I), first prepared by Hann and Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 2435) (who, however, did not provide experimental details), was obtained as follows. 3 : 4-Monoacetone 1 : 6-anhydro β-galactose was converted into 2-*methanesulphonyl* 3 : 4-*monoacetone* 1 : 6-*anhydro β-galactose*, mild acid hydrolysis of which gave 2-*methanesulphonyl* 1 : 6-*anhydro β-galactose* in good yield. The methanesulphonyl residue was readily removed by sodium methoxide at room temperature with formation of 2 : 3-1 : 6-dianhydro β-talose (I). 3 : 4-1 : 6-Dianhydro β-talose (II) was obtained by the method of Hann and Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 925).

By analogy with investigations on 2 : 3-anhydro β-methyltaloside it was expected that treatment of (I) with aqueous ammonia would give mainly 3-amino 1 : 6-anhydro β-idose (III) together with a small amount of 2-amino 1 : 6-anhydro β-galactose (IV). The results showed, however, that the action of ammonia gave (IV) (isolated as the crystalline *hydrochloride*) in 56% yield while (III) was formed in very low yield indeed and was obtained only in the form of its acetyl derivative, 3-*acetamido* 2 : 4-*diacetyl* 1 : 6-*anhydro β-idose* (VI).

Similarly when sodium methoxide was used to effect the scission of the 2 : 3-anhydro ring in (I), 2-methyl 1 : 6-anhydro β-galactose (VII), isolated as its *monoacetone* derivative (VIII), was obtained in 60% yield and no idose derivative could be isolated in the pure state. Thus considering the scission by alkaline reagents of the 2 : 3-anhydro ring in these talose derivatives it was clear that the β-1 : 6-anhydro ring exercised a directing influence different from that shown by the β-methyl glucosidic group; in the first case the entering anion (James *et al.*, *loc. cit.*) attaches itself mainly to C_2 and in the second case mainly to C_3 of the sugar molecule.

Clear proof of the constitutions of (III) and (IV) was obtained from a comparative study of the action of ammonia on the two isomeric dianhydrides (I) and (II). Treatment of (I) with ammonia under pressure, followed



by hydrolysis of the products with hydrochloric acid, yielded a crystalline hydrochloride, $[\alpha]_D^{22}$ −15·5°, and a residue which by acetylation gave a crystalline amino triacetyl anhydrohexose. The latter was also formed from (II) by the same reactions together with a second crystalline hydrochloride. Now on scission of the 2 : 3-anhydro ring in (I) by ammonia there should be obtained 2-amino 1 : 6-anhydro β-galactose (IV) and 3-amino 1 : 6-anhydro β-idose (III), while from (II) the ammonolysis products should be (III) and 4-amino 1 : 6-anhydro β-mannose (V). Thus the common amino triacetyl anhydrohexose above was undoubtedly a derivative of (III), *i.e.*, 3-acetamido 2 : 4-diacetyl 1 : 6-anhydro β-idose (VI), m. p. 245—246°, $[\alpha]_D^{20°}$ −71° in chloroform. The first hydrochloride was that of (IV) and the second hydrochloride was that of (V); the latter on acetylation gave 4-*acetamido* 2 : 3-*diacetyl* 1 : 6-*anhydro* β-*mannose*, m. p. 180°, $[\alpha]_D^{18°}$ −76° in chloroform, which was quite distinct from (VI).

On treatment of (II) with sodium methoxide there was obtained 4-methyl 1 : 6-anhydro β-mannose (IX) isolated as its 2 : 3-monoacetone derivative (X) in 60% yield. (IX) was identical with the substance obtained by methylation of 2 : 3-monoacetone 1 : 6-anhydro β-mannose (Hann and Hudson, *loc. cit.*). 3-Methyl 1 : 6-anhydro β-idose should also have been present in the reaction mixture, but so far it has not been identified.

The isolation and characterisation of 2-amino 1 : 6-anhydro β-galactose made possible the solution of an outstanding problem in carbohydrate chemistry, namely the precise configuration of chondrosamine, the naturally occurring amino sugar present in cartilagenous tissue. Since chondrosamine on treatment with phenylhydrazine (Levene, " Hexosamines and Mucoproteins," Longmans, Green and Co., London, 1925) gives galactosazone, it would appear to be either 2-amino galactose or 2-amino talose, a point which Levene (*loc. cit.*) demonstrated more strongly by his synthesis of chondrosamine by an " ascent of the series " from l-amino lyxose. If in fact chondrosamine is 2-amino galactose then hydrolysis of the 1 : 6-anhydro ring in 2-amino 1 : 6-anhydro galactose (IV), a scission which must occur without any configurational change in the molecule other than on C_1, will give chondrosamine. This hydrolysis was achieved using concentrated hydrochloric acid, and 2-amino galactose hydrochloride (XI) was obtained in well-formed crystals and good yield. It showed $[\alpha]_D$ +125°→+98° in one hour, a value identical with that of a specimen of chondrosamine hydrochloride prepared from bovine tracheal cartilage (Stacey, *J.*, 1944, 272). Complete identity of the synthetic material with chondrosamine hydrochloride was established by a comparison of their *X*-ray powder photographs. Finally 2-acetamido tetra-acetyl β-galactose, m. p. 238°, prepared from the synthetic material was identical with β-penta-acetyl chondrosamine (Stacey, *loc. cit.*).

The stability of the 1 : 6-anhydro ring in (IV) is of interest. Not only were more drastic conditions needed for hydrolysis by means of aqueous acid than is usual even for the methylated derivatives of 1 : 6-anhydro β-galactose (cf. McCreath and Smith, *J.*, 1939, 347), but attempted acetolysis of (IV) failed to achieve scission of the 1 : 6-anhydro ring.

Experimental.

2-*Methanesulphonyl* 3 : 4-*Monoacetone* β-1 : 6-*Anhydro Galactose*.—3 : 4-Monoacetone β-1 : 6-anhydro galactose (4·01 g.) (Hann and Hudson, *loc. cit.*) was dissolved in anhydrous pyridine (20 c.c.) and methanesulphonyl chloride (2·4 c.c.) was added drop by drop with shaking. After being kept overnight the crystalline mass which separated was transferred into

ice-cold water and the crystals (4·6 g.) collected, washed with water, and dried in a vacuum over phosphorus pentoxide. Recrystallisation from methyl alcohol gave 2-*methanesulphonyl* 3 : 4-*monoacetone* β-1 : 6-*anhydro galactose* (4·2 g.), m. p. 156°, $[\alpha]_D^{15°}$ −47° in chloroform (*c*, 1·6) (Found : C, 43·1; H, 6·0. $C_{10}H_{16}O_7S$ requires C, 42·8; H, 5·8%).

2-*Methanesulphonyl* β-1 : 6-*Anhydro Galactose*.—2-Methanesulphonyl 3 : 4-monoacetone β-1 : 6-anhydro galactose (6·8 g.) was boiled under reflux for seven hours with ethyl alcohol (250 c.c.) containing 0·5N-sulphuric acid (120 c.c.). After being kept overnight the solution was diluted with water and neutralised with barium carbonate. The solution was filtered and the residue washed repeatedly with hot water. The filtrate and washings were evaporated to dryness under reduced pressure and the residue extracted with boiling alcohol. Evaporation of the filtered extract gave a mass of crystals which on recrystallisation from ethyl alcohol gave 2-*methanesulphonyl* β-1 : 6-*anhydro galactose* (4·2 g.), m. p. 145°, $[\alpha]_D^{14°}$ −11° in methyl alcohol (*c*, 0·9) (Found : C, 35·5; H, 4·9; S, 13·2. $C_7H_{12}O_7S$ requires C, 35·0; H, 5·0; S, 13·3%).

2 : 3-1 : 6-*Dianhydro* β-*Talose*.—2-Methanesulphonyl β-1 : 6-anhydro galactose (3·04 g.) was dissolved in dry methyl alcohol (100 c.c.) and sodium methoxide (9·3 c.c. of 1·5 N-solution) was added to the cooled solution. The course of the reaction was followed polarimetrically : $[\alpha]_D^{18°}$ −11·5° (initial value); −26° (3 hrs.); −42° (16 hrs.); −43° (18·5 hrs.); −47° (63 hrs.; constant value). The solution was neutralised (litmus) and evaporated to dryness at 40° under reduced pressure. The residue was extracted with acetone and the filtered extract evaporated to a crystalline residue (1·9 g.). This was recrystallised from acetone–ether when 2 : 3-1 : 6-dianhydro β-talose (1 g.) was obtained, m. p. 132°, $[\alpha]_D^{20°}$ −88° in water (*c*, 0·76) (Found : C, 49·9; H, 5·5. Calc. for $C_6H_8O_4$: C, 50·0; H, 5·5%).

The Ammonolysis of 2 : 3-1 : 6-*Dianhydro* β-*Talose*.—Dianhydro talose (1·3 g.) was heated with ammonia (170 c.c.; *d* 0·880) in an autoclave at 100° for 30 hours. The solution was evaporated under reduced pressure in an atmosphere of nitrogen to give a syrup which was purified by treatment with charcoal in aqueous solution. Evaporation finally gave a syrup (1·52 g.) which partly crystallised.

In a previous experiment these crystals were separated by trituration with warm ethyl alcohol and recrystallised from *iso*propyl alcohol. They were 2-*amino* β-1 : 6-*anhydro galactose* and had m. p. 168—170°, $[\alpha]_D^{18°}$ −27·5° in water (*c*, 0·64) (Found : N, 8·8. $C_6H_{11}O_4N$ requires N, 8·7%).

The product was dissolved in alcohol, and N-hydrochloric acid (9·3 c.c.) added. The solution was evaporated to dryness and the solid residue recrystallised from aqueous methyl alcohol when the *hydrochloride* of 2-amino β-1 : 6-anhydro galactose (1·01 g.; 56% of the theoretical), m. p. 215° (decomp.), $[\alpha]_D^{22°}$ −15·5° in water (*c*, 2·2), was obtained (Found : C, 36·9; H, 6·1; N, 6·5; Cl, 17·6. $C_6H_{12}O_4NCl$ requires C, 36·4; H, 6·1; N, 7·1; Cl, 18·0%).

Examination of the Residual Syrup.—When all the crystalline 2-amino β-1 : 6-anhydro galactose hydrochloride had been separated the remaining syrup (0·59 g.) was dissolved in anhydrous pyridine (20 c.c.) and acetic anhydride (4 c.c.) was added. The reaction mixture was kept at room temperature for 5 days and was then poured into ice-cold water. The acetylated product was extracted with chloroform, the extract washed successively with ice-cold N-hydrochloric acid, water, sodium bicarbonate solution, and water. It was then dried ($MgSO_4$), filtered, and the solvent removed. The residue (0·61 g.) partly crystallised and the crystals (0·177 g.) were separated by trituration with alcohol. They were a mixture of 2-acetamido 3 : 4-diacetyl 1 : 6-anhydro β-galactose and 3-*acetamido* 2 : 4-*diacetyl* 1 : 6-*anhydro* β-*idose* (VI). Separation of the two was effected by fractional crystallisation from alcohol. The latter substance (30 mg.) had m. p. 246°, $[\alpha]_D^{23°}$ −70° in chloroform (*c*, 0·41) (Found : C, 50·0; H, 5·85; *O*-Ac, 44·8. $C_{12}H_{17}O_7N$ requires C, 50·2; H, 5·9; *O*-Ac, 44·9%), and the former (17 mg.) had m. p. 206° alone and in admixture with a specimen prepared by acetylation of the hydrochloride of (IV) (see below).

2-*Acetamido* 3 : 4-*Diacetyl* 1 : 6-*Anhydro* β-*Galactose*.—2-Amino 1 : 6-anhydro β-galactose hydrochloride (96 mg.) was dissolved in anhydrous pyridine (2 c.c.) and acetic anhydride (0·3 c.c.) was added. After keeping at room temperature for several days the solvent was distilled off under reduced pressure and the residue dissolved in chloroform. The solution was washed successively with cold dilute hydrochloric acid, sodium bicarbonate solution, and water. It was then dried ($MgSO_4$), filtered, and the solvent removed. The residue (85 mg.) was recrystallised from alcohol and was 2-*acetamido* 3 : 4-*diacetyl* 1 : 6-*anhydro* β-*galactose*, m. p. 207°, $[\alpha]_D^{13°}$ −73·5° in water (*c*, 0·74), $[\alpha]_D^{22°}$ −36° in chloroform (*c*, 0·55) (Found : C, 50·0; H, 5·7; *O*-Ac, 46·1. $C_{12}H_{17}O_7N$ requires C, 50·2; H, 5·9; *O*-Ac, 44·9%).

Attempted Acetolysis of 2-*Amino* 1 : 6-*Anhydro* β-*Galactose Hydrochloride*.—The material (0·152 g.) was placed in a flask and the ice-cold acetolysis mixture (4 c.c.) (35 c.c. acetic anhydride, 15 c.c. glacial acetic acid, 1 c.c. concentrated sulphuric acid) was added. The reaction mixture was allowed to stand at room temperature for 3 days, the solution cooled in ice, diluted with water, and carefully neutralised with sodium hydroxide solution (phenolphthalein). The solution was exhaustively extracted with chloroform, and the extract washed with water and dried ($MgSO_4$). Evaporation of the filtered extract gave a syrup (0·187 g.) which crystallised spontaneously. Recrystallisation from alcohol gave crystals having m. p. 208° alone and in admixture with the product from the previous experiment, and $[\alpha]_D^{13°}$ −74·2° in water (*c*, 0·3).

Hydrochloride of 2-*Amino Galactose*.—2-Amino 1 : 6-anhydro β-galactose (0·41 g.) was dissolved in 2·2N-hydrochloric acid (28 c.c.) and the solution boiled under reflux for 30 hours. The solution, filtered with the addition of charcoal, was evaporated under reduced pressure to give a white crystalline residue (0·35 g.), $[\alpha]_D^{23°}$ +108°. The product was dissolved in aqueous methyl alcohol and acetone was added to the hot solution. Needle-like crystals immediately began to separate. These were filtered off and washed with acetone. They had $[\alpha]_D^{23°}$ +125° changing to +98° in 1 hour and were 2-amino α-galactose hydrochloride (Found : C, 33·9; H, 6·62; N, 6·7; Cl, 17·2. Calc. for $C_6H_{14}O_5NCl$: C, 33·4; H, 6·54; N, 6·34; Cl, 16·5%). The specific rotation agrees well with that given for α-chondrosamine hydrochloride by Levene (*loc. cit.*). An *X*-ray powder photograph showed the identity of the synthetic with the naturally occurring compound (Stacey, *loc. cit.*).

2-*Acetamido* β-*Tetra-acetyl Galactose*.—The mother liquor from which the 2-amino α-galactose hydrochloride had been separated was evaporated to a syrup (0·267 g.) which was acetylated with acetic anhydride in pyridine. The product (0·413 g.) was partly crystalline. The crystals were separated by trituration with alcohol and recrystallised from alcohol and chloroform. The crystals had m. p. 238° alone and in admixture with β-penta-acetyl chondrosamine (Stacey, *loc. cit.*).

The Action of Ammonia on 3 : 4-1 : 6-*Dianhydro* β-*Talose*.—The dianhydride (2 g.) was heated with aqueous ammonia (*d* 0·88; 200 c.c.) in an autoclave for 48 hours. A clear yellow solution was obtained which after evaporation gave a yellow syrup (2·3 g.). This, dissolved in water (2 c.c.), was treated at 0° with concentrated hydrochloric acid (2 c.c.) until just acid. On the addition of alcohol prismatic crystals (A) separated (1·79 g.). The mother liquors were evaporated to give a brown syrup (B) (0·44 g.). The crystals (A) had no distinct m. p. but decomposed at 175—180°, $[\alpha]_D^{18°}$ −100·4° in water (*c*, 4·56) (no change in 24 hours) (Found : C, 36·0; H, 5·9; N, 7·1. $C_6H_{12}O_4NCl$ requires C, 36·4; H, 6·1; N, 7·1%). They were 4-*amino* β-1 : 6-*anhydro mannose hydrochloride*. Yield, 79·8% of the theoretical.

The syrup (B) (0·44 g.) was acetylated by boiling under reflux for 10 minutes with acetic anhydride (10 c.c.) and fused sodium acetate (0·5 g.). The cooled mixture was poured into ice-water, neutralised with sodium bicarbonate, and the solution extracted four times with chloroform. The extract was dried ($MgSO_4$) and evaporated. The syrupy product (0·2 g.) partly crystallised and on recrystallisation from alcohol prisms were obtained which showed $[\alpha]_D^{20°}$ −71·1° in

chloroform (*c*, 0·84) and had m. p. 245—246° alone and in admixture with 3-acetamido 2 : 4-diacetyl 1 : 6-anhydro β-idose previously isolated from the products of ammonolysis of (I). Yield, 30 mg. (0·75% of the theoretical) (Found : C, 50·0; H, 6·0%).

4-*Acetamido* 2 : 3-*Diacetyl* β-1 : 6-*Anhydro Mannose*.—4-Amino 1 : 6-anhydro mannose hydrochloride (0·18 g.) was refluxed for 15 minutes with acetic anhydride (3 c.c.) and fused sodium acetate (0·2 g.). The mixture was poured into ice-water, neutralised with sodium bicarbonate, and the solution extracted with chloroform. The extract was dried ($MgSO_4$), filtered, and evaporated to a syrup (0·23 g.) which rapidly crystallised on trituration with alcohol. The *compound* recrystallised from alcohol in clusters of stout needles, m. p. 180°, $[\alpha]_D^{18°}$ −76·0° in chloroform (*c*, 0·54) (Found : C, 50·2; H, 5·9; N, 5·3. $C_{12}H_{17}O_7N$ requires C, 50·2; H, 5·9; N, 4·9%).

Treatment of 2 : 3-1 : 6-*Dianhydro* β-*Talose with Sodium Methoxide*.—2 : 3-1 : 6-Dianhydro β-talose (0·76 g.) was dissolved in dry methyl alcohol (25 c.c.) containing sodium (1·2 g.) and the solution was boiled under reflux for 17 hours. The solution, which became too dark for the course of the reaction to be followed polarimetrically, was cooled and neutralised to litmus with dilute sulphuric acid. It was then filtered and evaporated to dryness under reduced pressure, and the residue taken up in methyl alcohol. Acetone and ether were added and inorganic impurities separated as a brown, flocculent precipitate leaving a clear yellow solution. This was filtered and the solvent distilled off giving a syrup (0·65 g.).

The product was dissolved in acetone (50 c.c.) and concentrated sulphuric acid (0·5 c.c.) was added. The solution was kept overnight, neutralised with anhydrous sodium carbonate, filtered, and evaporated to dryness under reduced pressure in the presence of a little barium carbonate. The residue was repeatedly extracted with ether; the extract on evaporation gave a syrup (A) (0·51 g.). Extraction of the residue with alcohol gave a syrup (B) (0·022 g.). The syrup (A) crystallised on nucleation with 2-methyl 3 : 4-monoacetone 1 : 6-anhydro β-galactose. The crystals were extracted with light petroleum and the extract evaporated. The product (0·32 g.), recrystallised from light petroleum, had m. p. 37° alone or in admixture with 2-methyl 3 : 4-monoacetone 1 : 6-anhydro β-galactose, $[\alpha]_D^{22}$ −72° in water (*c*, 1·2). The syrup (B) should contain 3-methyl 1 : 6-anhydro β-idose, but no crystalline derivative has as yet been obtained.

Methylation of 3 : 4-*Monoacetone* 1 : 6-*Anhydro* β-*Galactose*.—3 : 4-Monoacetone 1 : 6-anhydro β-galactose (1 g.) was methylated three times with methyl iodide and silver oxide. After the third methylation the product was recrystallised from light petroleum and was 2-*methyl* 3 : 4-*monoacetone* 1 : 6-*anhydro* β-*galactose* (0·71 g.), m. p. 37°, $[\alpha]_D^{18°}$ in water (*c*, 2·3) (Found : OMe, 15·0. $C_{10}H_{16}O_5$ requires OMe, 14·35%).

Action of Sodium Methoxide on 3 : 4-1 : 6-*Dianhydro* β-*Talose*.—The dianhydride (1 g.) was boiled under reflux with methyl alcohol (50 c.c.) containing sodium (0·75 g.) for 30 hours. Thereafter the solution was neutralised with N-sulphuric acid and evaporated to dryness in the presence of barium carbonate. The dry residue was extracted several times with boiling ethyl acetate and on evaporation of the extract a syrup (1·22 g.) was obtained. This was treated at room temperature with acetone (200 c.c.) containing concentrated sulphuric acid (1 c.c.) for 24 hours and then the solution was neutralised with sodium carbonate, filtered, the residue washed with acetone, and the filtrate and washings evaporated to dryness. The syrupy product was extracted with light petroleum, leaving a residue (B) (0·36 g.) which should contain 3-methyl 1 : 6-anhydro β-idose but from which no crystalline material has so far been obtained. The light petroleum solution, on evaporation gave a syrup (A) (0·8 g.) which crystallised completely. On recrystallisation from ether–light petroleum it gave crystals (0·62 g.) of 4-methyl 2 : 3-monoacetone 1 : 6-anhydro β-mannose which showed $[\alpha]_D^{20°}$ −34·4° in chloroform (*c*, 1·6) and had m. p. 53° alone and in admixture with a specimen obtained by methylation of 2 : 3-monoacetone 1 : 6-anhydro β-mannose according to Hann and Hudson (*loc. cit.*). This specimen had $[\alpha]_D^{20°}$ −33·1° in chloroform (*c*, 1·2) and m. p. 53°, in agreement with the values $[\alpha]_D$ −33·4° in chloroform and m. p. 53—54° recorded by Hann and Hudson.

The authors wish to express their thanks to Professor W. N. Haworth, F.R.S., for his interest in this work, and also to Dr. F. J. Llewellyn for *X*-ray powder photographs.

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[*Received, December 20th*, 1945.]