135. *Sugar Nitrates. Part I. Syntheses of* 2 : 4-*Dimethyl* β-*Methylglucoside and* 2 : 4 : 6-*Trimethyl* β-*Methylglucoside.*

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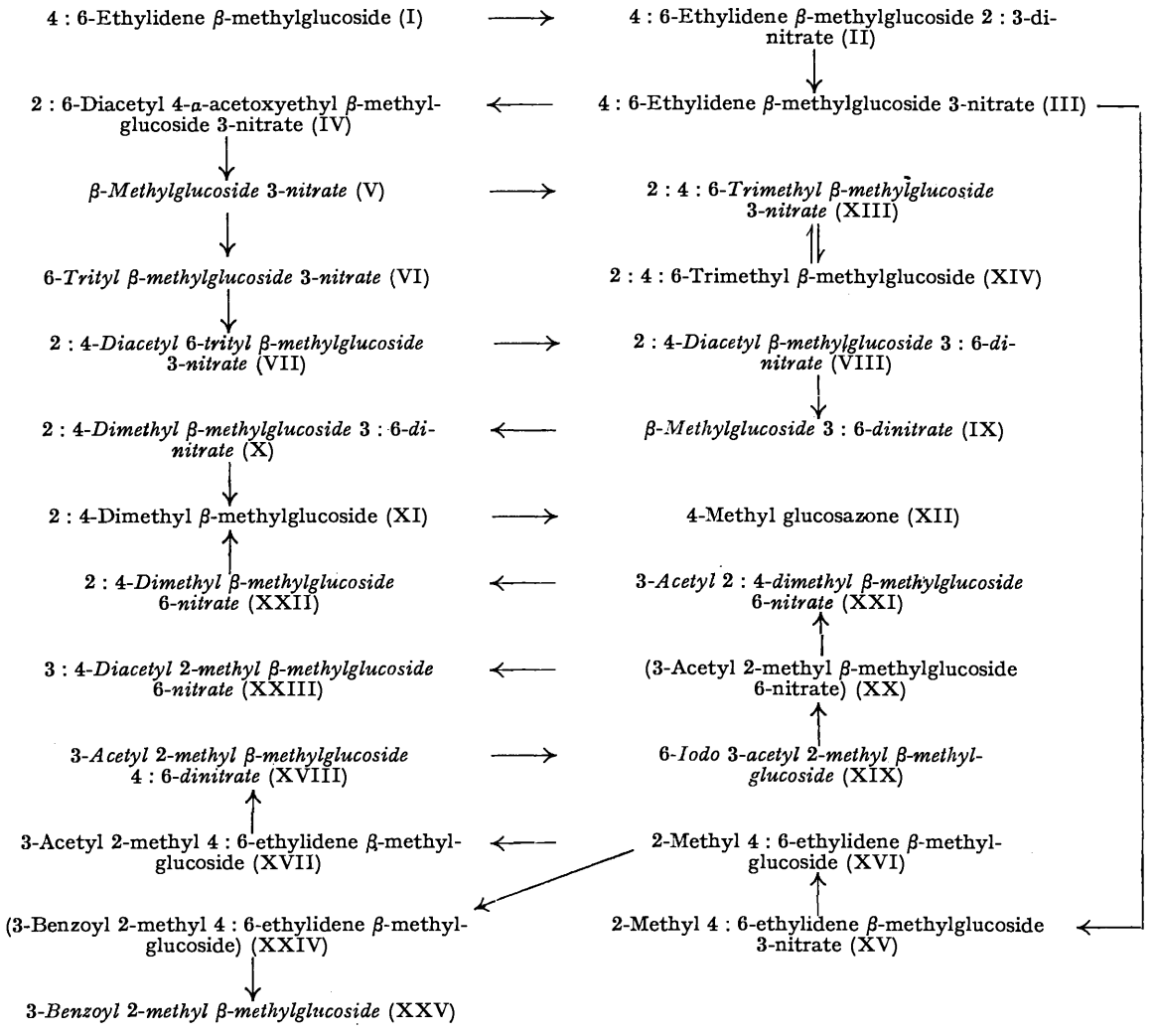
Two syntheses of 2 : 4-dimethyl β-methylglucoside and one of 2 : 4 : 6-trimethyl β-methylglucoside, all originating from 4 : 6-ethylidene β-methylglucoside 2 : 3-dinitrate, are described: these illustrate the uses of nitration and denitration and allied processes in this field. Details are given of a number of new derivatives, mainly nitrates, of β-methylglucoside.

THE experiments recorded here and in the following two papers were undertaken with a view to complete the series of partly methylated glucopyranoses, of which the 2 : 4-dimethyl and the 3 : 4-dimethyl derivative were unknown; subsequently, two syntheses of 2 : 4-dimethyl β-methylglucoside were described by Reeves, Adam, and Goebel (*J. Biol. Chem.*, 1941, **140**, 653), who also showed that the dimethyl methylglucoside isolated by Robertson and Waters (J., 1931, 1707) was, in fact, 2 : 4-dimethyl α-methylglucoside.

The nitration of 4 : 6-benzylidene β-methylglucoside was found by Oldham (*J. Soc. Chem. Ind.*, 1934, **53**, 236T) to promote the simultaneous formation of a nitrobenzylidene substituent in addition to the introduction of nitrate groups into positions 2 and 3, and this nitrobenzylidene residue could not subsequently be removed by normal hydrolysis processes. Use of 4 : 6-ethylidene β-methylglucoside (Helferich and Appel, *Ber.*, 1931, **64**, 1841) in place of the corresponding benzylidene compound avoided the complication of substituent nitration, and Oldham was able to remove preferentially one of the two nitrate groups. Later, one of us (J. D.), in collaboration with Oldham (unpublished result), repeated this work and showed that the dinitrate on treatment with sodium iodide in acetone (cf. Bell and Synge, J., 1937, 1711; 1938, 833) gave 4 : 6-ethylidene β-methylglucoside 3-nitrate. From this compound various routes towards 2 : 4-dimethyl β-methylglucoside suggested themselves: two of these were completed, and a number of intermediate and subsidiary compounds (mainly nitrates) of value for reference purposes were isolated and characterised. The various steps are shown in the table.

Modification of the processes described by Helferich and Appel (*loc. cit.*) and by Appel and Haworth (J., 1938, 793) gave almost quantitative conversion of β-methylglucoside into 4 : 6-ethylidene β-methylglucoside (I), which, under the conditions employed by us, was largely formed in preference to the subsidiary product 2 : 3-oxidodiethylidene 4 : 6-ethylidene β-methylglucoside. Nitration of (I) gave rise to different products according to the method adopted: in the normal process, using a mixture of chloroform and fuming nitric acid at 0° (cf. Oldham, J., 1925, **127**, 2840, *et seq.*), removal of the ethylidene residue took place as well as



(Compounds in parenthesis have not been characterised.)

the introduction of nitrate groups, the product being β-methylglucoside 2 : 3 : 4 : 6-tetranitrate (Part III), whereas application of the alternative method developed by Oldham (cf. Bell and Synge, *loc. cit.*), in which a non-acidic solution of dinitrogen pentoxide in chloroform is used, produced no substantial removal of the ethylidene group.

For the removal of the 2-nitrate group from (II), Bell and Synge (*loc. cit.*) advocate a period of heating with sodium iodide and acetone of only 1 hour, but we found that a period of about 20 hours was necessary, preferably with cooling and release of pressure after 10 hours. By these means we were able to obtain consistently pure 4 : 6-ethylidene β-methylglucoside 3-nitrate (III) in 40% of the theoretical amount. Removal of the ethylidene residue to give (IV), followed by alkaline hydrolysis [cf. Gladding and Purves, *J. Amer. Chem. Soc.*, 1944, **66**, 76, 153), gave β-*methylglucoside* 3-*nitrate* (V), the structure of which was further confirmed by methylation to 2 : 4 : 6-*trimethyl* β-*methylglucoside* 3-*nitrate* (XIII), which, on removal of the nitrate group, gave the known 2 : 4 : 6-trimethyl β-methylglucoside (XIV) (Oldham, *J. Amer. Chem. Soc.*, 1934, **56**, 1360; Freudenberg and Plankenhorn, *Annalen*, 1938, **536**, 257; Lake and Peat, J., 1938, 1417). Incidentally, these processes provide a convenient method for the preparation of 2 : 4 : 6-trimethyl β-methylglucoside.

The mononitrate (V) condensed readily with trityl chloride in anhydrous pyridine to give the 6-*trityl* compound (VI), which, though itself non-crystalline, gave crystalline 2 : 4-*diacetyl* 6-*trityl* β-*methylglucoside* 3-*nitrate* (VII). Treatment with fuming nitric acid in chloroform gave a mixture of 2 : 4-*diacetyl* β-*methylglucoside* 3 : 6-*dinitrate* (VIII) and tritylcarbinol: separation of the constituents was not attempted at this stage, but after deacetylation by the Zemplen method crystalline β-*methylglucoside* 3 : 6-*dinitrate* (IX) was obtained by extraction of the carbinol with benzene from aqueous solution. Methylation readily gave 2 : 4-*dimethyl* β-*methylglucoside* 3 : 6-*dinitrate* (X), from which the nitrate residues were removed, giving

crystalline 2 : 4-dimethyl β-methylglucoside (XI). This substance had characteristics in agreement with those quoted by Adams, Reeves, and Goebel (*loc. cit.*), and, after hydrolysis, gave 4-methylglucosazone.

In the second main synthesis, 4 : 6-ethylidene β-methylglucoside 3-nitrate was converted into the 2-methyl compound (XV) from which the nitrate group could be removed to give 2-methyl 4 : 6-ethylidene β-methylglucoside (XVI). Acetylation gave 3-acetyl 2-methyl 4 : 6-ethylidene β-methylglucoside (XVII), and from this, by treatment with fuming nitric acid in the cold, 3-*acetyl* 2-*methyl* β-*methylglucoside* 4 : 6-*dinitrate* (XVIII) was obtained in good yield. Denitration of this with simultaneous introduction of iodine into the 6-position (cf. Oldham and Rutherford, *J. Amer. Chem. Soc.*, **1932**, **54**, 366) gave 6-*iodo* 3-*acetyl* 2-*methyl* β-*methylglucoside* (XIX), again in good yield.

It seemed possible that the presence of iodine in position 6 might lead to complications if methylation were attempted by Purdie's method, and therefore the corresponding 6-nitrate (XX) was prepared; this was non-crystalline but readily gave rise to the crystalline *diacetyl* derivative (XXIII). Conversion by methylation into (XXI) and subsequent deacetylation to (XXII) gave a syrup in each case, but in the final stage, the removal by reduction of the nitrate group from (XXII), a good yield of 2 : 4-dimethyl β-methylglucoside, identical with the previous product, was obtained. The intermediate syrups (XXI) and (XXII) were probably not pure, some acyl migration having taken place during methylation.

In a subsidiary experiment, (XVI) was benzoylated, giving a syrup, essentially 3-benzoyl 2-methyl 4 : 6-ethylidene β-methylglucoside (XXIV), and it is noteworthy that subsequent treatment of this derivative with 1% hydrochloric acid served to remove the ethylidene group, giving a crystalline product, presumably 3-*benzoyl* 2-*methyl* β-*methylglucoside* (XXV).

Experimental.

All evaporations were carried out under diminished pressure and, unless otherwise stated, at below 50°. The light petroleum used in recrystallisations was of b. p. 60—80°.

4 : 6-*Ethylidene* β-*Methylglucoside* (I).—β-Methylglucoside (50 g.), paraldehyde (180 c.c.; dried over calcium chloride), concentrated sulphuric acid (0·44 c.c.), and some 20 small glass beads were shaken together for 48 hours, after which the solid portion (30 g.) of the reaction mixture was filtered off, washed twice with light petroleum, and recrystallised twice from methylated spirit, giving 4 : 6-ethylidene β-methylglucoside (m. p. 185—186°) pure enough for nitration. The paraldehyde filtrate gave 2 : 3-oxidodiethylidene 4 : 6-ethylidene β-methylglucoside (1—2 g.), which was converted into more 4 : 6-ethylidene β-methylglucoside by Appel and Haworth's method (*loc. cit.*). Utilisation of recovered materials in subsequent preparations made the conversion almost quantitative.

4 : 6-*Ethylidene* β-*Methylglucoside* 2 : 3-*Dinitrate* (II).—This was prepared by Oldham's method (unpublished result) [compare Bell and Synge (*loc. cit.*)]. Good yields (average 75%) were obtained by using not more than 3 g. of 4 : 6-ethylidene β-methylglucoside; on a larger scale the yield was considerably diminished. In practice, 8—10 samples were nitrated separately, and the combined chloroform extracts purified.

4 : 6-*Ethylidene* β-*Methylglucoside* 3-*Nitrate* (III).—The dinitrate (II) (10 g.), sodium iodide (20 g.), and acetone (70 c.c.) were heated in a sealed tube (capillary end) for 10 hours in a boiling water-bath. After cooling (overnight), the internal gas pressure was released by carefully fusing the fine capillary end with a small flame, the tube resealed, and heating continued for a further 10 hours. After cooling (overnight), the solvent was removed by distillation, and the residue shaken with chloroform and water. The chloroform layer was shaken in turn with sodium thiosulphate solution and with potassium hydrogen carbonate solution, and, after drying with sodium sulphate and simultaneously decolorising with norit, the solvent was removed by distillation. The crystalline residue was recrystallised from ethyl alcohol–light petroleum (2 : 1), giving (III) (8·6 g.) fine needles, m. p. 147°, $[\alpha]_D^{18°}$ −31·1° (chloroform, $l = 2$, $c = 1·6$).

2 : 6-*Diacetyl* 4-α-*Acetoxyethyl* β-*Methylglucoside* 3-*Nitrate* (IV).—The compound (III) (10 g.), on treatment with acetic anhydride (300 c.c.) and sulphuric acid (0·2 c.c.) (cf. Bell and Synge, *loc. cit.*), yielded a syrup (14·4 g.) from which crystals (6·3 g.), m. p. 125—126°, were obtained (*ex* ethyl alcohol and light petroleum).

β-*Methylglucoside* 3-*Nitrate* (V).—Methyl alcohol (62 c.c.) containing sodium methoxide (0·075 g. of sodium) was added to a solution of (IV) (6·2 g.) in chloroform (62 c.c.), and the course of the reaction followed polarimetrically, a constant value [$\alpha_D = -1·77°$ ($l = 2$)] being reached in 20 mins. Glacial acetic acid (0·184 c.c.) was then added, the solvent removed by distillation, the residue extracted with acetone, and the solvent distilled from this extract. A solution of the resultant glass (3·8 g.) in water was shaken thrice with chloroform, and subsequent evaporation of the aqueous solution gave a residue, from which by extraction with acetone and subsequent evaporation was obtained a glass (3·6 g.). Recrystallisation from water gave the product, m. p. 104—106°, $[\alpha]_D^{13°}$ −16·8° (ethyl alcohol, $l = 2$, $c = 5·222$) (Found: C, 35·0; H, 5·6; N, 6·0; OMe, 12·9. $C_7H_{13}O_8N$ requires C, 35·1; H, 5·4; N, 5·9; OMe, 13·0%).

6-*Trityl* β-*Methylglucoside* 3-*Nitrate* (VI).—The compound (V) (3·5 g.) and trityl chloride (3·93 g.) in dry pyridine (15 c.c.) were heated for 1 hour in a stoppered flask at 100° and thereafter poured into water (300 c.c.); the resulting gum was dissolved in benzene, and washed with 2% sulphuric acid, then 2% sodium hydroxide, and finally water. After drying (sodium sulphate), the solvent was distilled off, giving a glass in quantitative yield (Found: OMe, 5·7. $C_{26}H_{27}O_8N$ requires OMe, 6·4%). For the characterisation of the compound, purer material was obtained from the deacetylation of (VIII) (below); a solution of this compound (0·967 g.) in chloroform (15 c.c.) was treated in the cold with methyl alcohol in which sodium (9 mg.) had been dissolved. The progress of the reaction was followed polarimetrically, and after 40 hours the calculated amount of glacial acetic acid (0·022 c.c.) was added, and the solvent distilled off. The residue was treated with chloroform and the resulting solution washed with potassium hydrogen carbonate solution. The chloroform solution was dried (sodium sulphate), and removal of the solvent gave a colourless glass (0·832 g.) which softened at about 65° and showed $[\alpha]_D^{13°}$ −22·3° (chloroform, $l = 2$, $c = 3·612$) (Found: C, 64·8; H, 5·6; N, 2·9; OMe, 6·1. $C_{26}H_{27}O_8N$ requires C, 64·9; H, 5·6; N, 2·9; OMe, 6·4%).

2 : 4-*Diacetyl* 6-*Trityl* β-*Methylglucoside* 3-*Nitrate* (VII).—Acetylation in the usual manner of a sample of (VI) (2·469 g.), obtained from (V) as above, yielded 2·479 g. of crystals, which were recrystallised from ethyl alcohol. The pure *nitrate* (needles) had m. p. 161—162°, $[\alpha]_D^{15°}$ +23·9° (chloroform, $l = 2$, $c = 4·203$) (Found: C, 63·8; H, 5·4; N, 2·5; OMe, 5·4. $C_{30}H_{31}O_{10}N$ requires C, 63·7; H, 5·5; N, 2·5; OMe, 5·5%).

2 : 4-*Diacetyl* β-*Methylglucoside* 3 : 6-*Dinitrate* (VIII).—The compound (VII) (2 g.), dissolved in chloroform (20 c.c.), was cooled in ice, and a cold solution of fuming nitric acid (20 c.c.) in chloroform (20 c.c.) added. After 10 minutes at 0° the reaction was arrested by shaking quickly with ice and water, and then with a dilute solution of potassium hydrogen carbonate. After drying (sodium sulphate), the solvent was distilled off, giving a glass (2·27 g.) comprising (VIII) admixed with a small amount of tritylcarbinol. Separation of these constituents proved difficult at this stage,

and, a more effective separation being possible after deacetylation (see below), the impure material was used for the next stage. The pure *compound* [m. p. 78—79° (*ex* ethyl alcohol); $[\alpha]_D^{17°}$ −16·3° (chloroform, $l = 1$, $c = 2·14$)] was obtained by acetylation of (IX) (below) (Found: C, 36·3; H, 4·6; OMe, 8·1. $C_{11}H_{16}O_{12}N_2$ requires C, 35·9; H, 4·4; OMe, 8·4%).

β-Methylglucoside 3 : 6-*Dinitrate* (IX).—The dinitrate (VIII) (4·5 g.) in chloroform (45 c.c.) was treated with methyl alcohol containing sodium methoxide (0·036 g. of sodium) at room temperature for 5½ hours, the rotation then having become constant. Glacial acetic acid (0·094 c.c.) was added, and the solution evaporated to dryness. The crude product was extracted from this residue with chloroform–acetone, and, after removal of these solvents by distillation, was dissolved in water. From the aqueous solution the admixed tritylcarbinol was removed by three extractions with benzene, and the water thereafter distilled off. The crystalline residue was extracted with acetone, and, after decolorising (norit), the solvent was distilled off, giving a colourless crystalline product (1·816 g.). Recrystallisation from chloroform gave needles, m. p. 144—145°, $[\alpha]_D^{14°}$ −7·8° (acetone, $l = 2$, $c = 3·8$) (Found: C, 30·2; H, 4·3; OMe, 11·0. $C_7H_{12}O_{10}N_2$ requires C, 29·6; H, 4·2; OMe, 10·9%).

2 : 4-*Dimethyl β-Methylglucoside* 3 : 6-*Dinitrate* (X).—After two treatments with methyl iodide and silver oxide the above substance (IX) (0·757 g.) gave a clear syrup (0·831 g.), $n_D^{13°}$ 1·4645, $[\alpha]_D^{13°}$ −7·1° (chloroform, $l = 2$, $c = 4·2$) (Found: N, 9·4; OMe, 29·8. $C_9H_{16}O_{10}N_2$ requires N, 9·0; OMe, 29·8%).

2 : 4-*Dimethyl β-Methylglucoside* (XI).—(*a*) The *dinitrate* (X) (0·536 g.) in glacial acetic acid (6 c.c.) was treated with an excess of a mixture of zinc and iron powder with gentle heat until a test drop gave no blue coloration with diphenylbenzidine in sulphuric acid. Isolation was effected by filtration (the residues being washed with chloroform), adding the filtrate to a concentrated solution of potassium carbonate, extracting the aqueous mixture 12 times with chloroform, drying (sodium sulphate), and decolorising (norit) the chloroform solution and distilling off the solvent. The crystalline product (0·408 g.) gave fine needles from light petroleum–ethyl alcohol; m. p. 124—125°, $[\alpha]_D^{14°}$ −16·3° (acetone, $l = 2$, $c = 3·074$), $[\alpha]_D^{14°}$ −22·1° (ethyl alcohol, $l = 2$, $c = 3·075$) [cf. Adams, Reeves, and Goebel, *loc. cit.*; m. p. 122—124°, $[\alpha]_D^{29°}$ −18·6° (acetone, $c = 1·4$)] (Found: C, 48·8; H, 8·1; OMe, 41·8. Calc. for $C_9H_{18}O_6$: C, 48·7; H, 8·1; OMe, 41·8%).

A sample (0·092 g.) was hydrolysed with hot aqueous N-hydrochloric acid (10 c.c.), and the resultant syrup (0·08 g.) in water (3 c.c.) was heated on a water-bath for 2½ hours with sodium acetate (0·3 g.) and phenylhydrazine hydrochloride (0·19 g.). On cooling, 4-methyl glucosazone (XII) was deposited: m. p. 157—158° (from benzene–ethyl alcohol) [cf. Schinle (*Ber.*, 1932, **65**, 315), m. p. 159°; Munro and Percival (J., 1935, 873), m. p. 158°].

(*b*) The nitrate (XXII) (see below) (0·242 g.) was treated with glacial acetic acid (4 c.c.) and an excess of a mixture of zinc and iron powders. Isolation in the manner described above gave a syrup (0·228 g.), free from nitrate (diphenylbenzidine test), which crystallised on standing. Recrystallisation from light petroleum–ethyl alcohol gave needles, m. p. 124°, not depressed on mixing with a sample of the product obtained in (*a*); $[\alpha]_D^{16°}$ −16·6° (acetone, $l = 2$, $c = 4·16$).

2 : 4 : 6-*Trimethyl β-Methylglucoside* 3-*Nitrate* (XIII).—The compound (V) (1·885 g.) in dry acetone (10 c.c.) was given 2 treatments in the standard manner with methyl iodide (10 c.c.) and silver oxide (10 g.). A sample (1·44 g.) of the resultant syrup, $[\alpha]_D^{13°}$ −22·1° (chloroform, $l = 2$, $c = 7·225$), gave a colourless viscous liquid (1·12 g.) on distillation, b. p. 115—120°/0·4 mm.; $n_D^{16°}$ 1·4538; $[\alpha]_D^{15°}$ −22·0° (chloroform, $l = 2$, $c = 5·526$) (Found: C, 43·0; H, 6·7; N, 5·2. $C_{10}H_{19}O_8N$ requires C, 42·7; H, 6·8; N, 5·0%).

2 : 4 : 6-*Trimethyl β-Methylglucoside* (XIV).—The nitrate (XIII) (3·69 g.) was reduced by 45 mins.' refluxing with 2N-sodium hydroxide (30 c.c.) of which half had previously been saturated with hydrogen sulphide, sufficient ethyl alcohol being added to give homogeneity. The alcohol was removed by distillation, and water added to the residue, the resultant solution being then extracted 3 times with chloroform. The chloroform solution after drying (sodium sulphate), decolorisation (norit), and distillation gave a crystalline product (2·96 g.); silky needles (from light petroleum); m. p. 70°; $[\alpha]_D^{15°}$ −27·4° (chloroform, $l = 2$, $c = 0·7285$) (Found: C, 50·7; H, 8·3; OMe, 52·1. Calc. for $C_{10}H_{20}O_6$: C, 50·8; H, 8·5; OMe, 52·5%) [cf. Oldham (*J. Amer. Chem. Soc.*, 1934, **56**, 1360), Freudenberg and Plankenhorn (*Annalen*, 1938, **536**, 257), Lake and Peat (J., 1938, 1417)].

Nitration of (XIV) (0·519 g.) in chloroform (10 c.c.) with an ice-cold mixture of fuming nitric acid (10 c.c.) and chloroform (10 c.c.) for 10 minutes at 0°, followed by isolation as for (II), gave a thin syrup (0·543 g.) having $n_D^{14°}$ 1·4540.

2-*Methyl* 4 : 6-*Ethylidene β-Methylglucoside* 3-*Nitrate* (XV).—The compound (III) (5 g.) was completely methylated after one treatment (2 hours) in acetone (5 c.c.) with methyl iodide (10 c.c.) and silver oxide (10 g.). The product (5·27 g.) had m. p. 104—106° (from ethyl alcohol) (Bell and Synge, *loc. cit.*, give m. p. 104·5—105·5°) (Found: OMe, 22·1. Calc. for $C_{10}H_{17}O_8N$: OMe, 22·2%).

2-*Methyl* 4 : 6-*Ethylidene β-Methylglucoside* (XVI).—The above nitrate (XV) (4 g.) was treated with 2N-sodium sulphide solution (30 c.c.) as for (XIV), and the product (3·41 g.) had m. p. 120° (from ethyl alcohol), $[\alpha]_D^{15°}$ −66·8° (chloroform, $l = 2$, $c = 1·60$) (Bell and Synge, *loc. cit.*, give m. p. 122—123°, $[\alpha]_D$ −66·0°) (Found: C, 51·4; H, 7·8; OMe, 26·6. Calc. for $C_{10}H_{18}O_6$: C, 51·3; H, 7·7; OMe, 26·5%).

3-*Acetyl* 2-*Methyl* 4 : 6-*Ethylidene β-Methylglucoside* (XVII).—The glucoside (XVI) (1·75 g.) on treatment with acetic anhydride (1·15 g.) in anhydrous pyridine in the cold for 12 hours gave crystals (1·6 g.), m. p. 113° (from aqueous methyl alcohol), $[\alpha]_D^{18°}$ −34·8° (chloroform, $l = 2$, $c = 3·01$) (Found: C, 51·9; H, 6·9; OMe, 22·1. $C_{12}H_{20}O_7$ requires C, 52·1; H, 7·2; OMe, 22·4%).

3-*Acetyl* 2-*Methyl β-Methylglucoside* 4 : 6-*Dinitrate* (XVIII).—The *acetyl* derivative (XVII) (1·4 g.) in dry chloroform (20 c.c.) was treated for 15 minutes at 0° with fuming nitric acid (20 c.c.) in chloroform (20 c.c.). The product (1·4 g.), after isolation as for (VIII), had m. p. 73—75° (from ethyl acetate), $[\alpha]_D^{14°}$ +20·6° (chloroform, $l = 2$, $c = 4·126$) (Found: C, 35·8; H, 4·9; OMe, 18·7. $C_{10}H_{16}O_{11}N_2$ requires C, 35·3; H, 4·7; OMe, 18·2%).

6-*Iodo* 3-*Acetyl* 2-*Methyl β-Methylglucoside* (XIX).—The *dinitrate* (XVIII) (5·561 g.) was heated with sodium iodide and acetone (35 c.c.) in a sealed tube for 16 hours at 100°. The product (5·69 g.), isolated as for (III), crystallised from light petroleum–ether (2 : 1), showing m. p. 96—97°, $[\alpha]_D^{14°}$ +19·8° (chloroform, $l = 2$, $c = 5·22$) (Found: C, 33·5; H, 4·8; I, 34·8; OMe, 17·2. $C_{10}H_{17}O_6I$ requires C, 33·3; H, 4·7; I, 35·3; OMe, 17·2%).

3-*Acetyl* 2-*Methyl β-Methylglucoside* 6-*Nitrate* (XX).—A solution in acetonitrile (20 c.c.) of the *iodo*-compound (XIX) (1·059 g.) and silver nitrate (1·2 g.) was refluxed for 2 hours; the acetonitrile was then removed by distillation, and the residue extracted several times with boiling chloroform. Removal of the solvent by distillation gave a syrup, in theoretical amount; $n_D^{16°}$ 1·4650; $[\alpha]_D^{13°}$ +1·1° (chloroform, $l = 2$, $c = 4·21$). Acetylation of a sample (0·191 g.) yielded 3 : 4-*diacetyl* 2-*methyl β-methylglucoside* 6-*nitrate* (XXIII) (0·112 g.), needles (from light petroleum), m. p. 104—105°, $[\alpha]_D^{10°}$ +9·7° (chloroform, $l = 2$, $c = 1·536$) (Found: C, 42·7; H, 5·6; N, 4·0; OMe, 18·5. $C_{12}H_{19}O_{10}N$ requires C, 42·8; H, 5·6; N, 4·1; OMe, 18·4%).

3-*Acetyl* 2 : 4-*Dimethyl β-Methylglucoside* 6-*Nitrate* (XXI).—After 2 treatments with Purdie's reagents the above compound (XX) (0·407 g.) gave a syrup (0·418 g.) which had $n_D^{19°}$ 1·4550, $[\alpha]_D^{16°}$ −5·7° (chloroform, $l = 2$, $c = 4·15$) (Found: OMe, 30·3. $C_{11}H_{19}O_9N$ requires OMe, 30·1%).

2 : 4-*Dimethyl β-Methylglucoside* 6-*Nitrate* (XXII).—Deacetylation of the foregoing *compound* by Zemplen's method proceeded very slowly. The compound (0·415 g.) in chloroform (10 c.c.) was treated with methyl alcohol (10 c.c.) containing sodium methoxide (10 mg. of sodium), the course of the reaction being followed polarimetrically. When a constant value was reached (6 days) the product was isolated in the standard manner as a syrup (0·315 g.) which could not be crystallised. It had $n_D^{18°}$ 1·4630, $[\alpha]_D^{14°}$ −15·2° (chloroform, $l = 2$, $c = 3·15$) (Found: OMe, 35·0. $C_9H_{17}O_8N$ requires OMe, 34·8%).

3-*Benzoyl* 2-*Methyl β-Methylglucoside* (XXV).—A sample of (XVI) (0·279 g.) on treatment with benzoyl chloride (0·42 c.c.) in pyridine yielded a colourless syrup (XXIV) (0·51 g.) which could not be crystallised. A mixture of this compound (0·5 g.) and aqueous alcohol (25 c.c.) containing 1% hydrochloride acid was heated under reflux for 5 hours (*i.e.*, until of constant rotation); barium carbonate was added to neutralise the acid, and, after filtration, the alcohol was removed by distillation. The residual aqueous solution was further diluted with water, and shaken twice with benzene, the extract being discarded. Much potassium chloride was then added, and the solution shaken 6 times with chloroform. After drying (sodium sulphate), the solvent was removed by distillation from the combined chloroform extracts, yielding a syrup (0·332 g.) which crystallised after some hours in contact with ether–light petroleum. Recrystallisation from benzene–light petroleum gave plates, m. p. 132—133°, $[\alpha]_D^{14°}$ +28·5° (chloroform, $l = 2$, $c = 1·42$) (Found: C, 57·7; H, 6·6; OMe, 20·2. $C_{15}H_{20}O_7$ requires C, 57·7; H, 6·4; OMe, 19·9%).

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