# 136. *Sugar Nitrates. Part II. Synthesis of* 3 : 4-*Dimethyl Glucose :* 3-*Methyl* β-*Methylglucoside.*

By JOHN DEWAR and GODFREY FORT.

Starting from 4 : 6-ethylidene β-methylglucoside 3-nitrate, a simple synthesis of 3 : 4-dimethyl glucose was accomplished, thus completing the series of partly methylated glucoses. From the same compound, by three routes, the known 3-methyl β-methylglucoside was also obtained. A number of new derivatives of β-methylglucoside are described.

IN proceeding from 4 : 6-ethylidene β-methylglucoside 3-nitrate towards a synthesis of 3 : 4-dimethyl glucose, the 2-benzoyl derivative (I) and thence 2-benzoyl 4 : 6-ethylidene β-methylglucoside (II) were first formed. Choice of benzoyl in preference to acetyl derivatives was based on the possibility of acyl migration during methylation : this disadvantage was found to outweigh the advantages attending the use of acetyl derivatives, in that it was found that methylation of 2-acetyl 4 : 6-ethylidene β-methylglucoside (XX) failed to give a definite crystalline compound, although subsequently by other means (III ⟶ XVI ⟶ XVIII) this could be obtained. Tosyl compounds provided another alternative, but, although a series of definite crystalline tosyl derivatives (XXI, XXII, XXIII) was obtained, the route was not fully explored.

In the series of reactions described, removal of the ethylidene residue was effected in three different ways : (*a*) acid hydrolysis [(cf., *inter alia*, Ohle and Spencker, *Ber.*, **1928**, **61**, 2387), (III) ⟶ (IV); (*b*) acetolysis (cf. Bell and Synge, J., **1937**, 1711), (III) ⟶ (XIII); (*c*) by the use of fuming nitric acid in chloroform, (XVI) ⟶ (XVII). Method (*a*), although applicable to this class of compound [see preceding paper, (XXIV) ⟶ (XXV)], is unsuitable for ethylidene compounds having the nitrate group in position 2 or 3 (cf. Bell and Synge, *loc. cit.*). In earlier work we found that the process was effective in the case of 2-methyl ethylidene β-methylglucoside, but very slow. The syrup obtained from (III) by the use of method (*b*) was, by analogy to similar cases (Bell and Synge, *loc. cit.*), deemed to be (XIII), and gave the expected 3-methyl β-methylglucoside (XIV) on alkaline hydrolysis. The syrupy nature of the product of this reaction is in accordance with frequent experience, for our attempts to apply the reaction to a large number of ethylidene compounds have, with the exception of those described by Bell and Synge, failed to give crystalline compounds. It is noteworthy that treatment of 2-methyl 4 : 6-ethylidene β-methylglucoside 3-nitrate in this way gave a syrup, but that after some months crystals were deposited, which were however ineffective in inducing the crystallisation of a freshly prepared syrup. Analytical data for the crystalline deposit corresponded to a monoacetyl monomethyl β-methylglucoside 3-nitrate, presumably 6-*acetyl* 2-*methyl* β-*methylglucoside* 3-*nitrate* formed by decomposition of the syrup with elimination of the 4-α-acetoxyethyl group. Method (*c*) in general replaces the ethylidene group by two nitrate groups, at the same time introducing further nitrate substituents where places are available.

Complete absence of steric effect exerted by the triphenylmethyl group was observed, methylation of (V) to (VI) being effected in one treatment.

The identity of (IX) seems conclusive. It differs from the known dimethyl β-methylglucosides and therefore must be the 3 : 4-isomer, the only remaining possibility. This is in accordance with the method of synthesis, wherein, by the formation of 3-methyl β-methylglucoside by two routes from (III), the position of one of the methyl groups is confirmed.

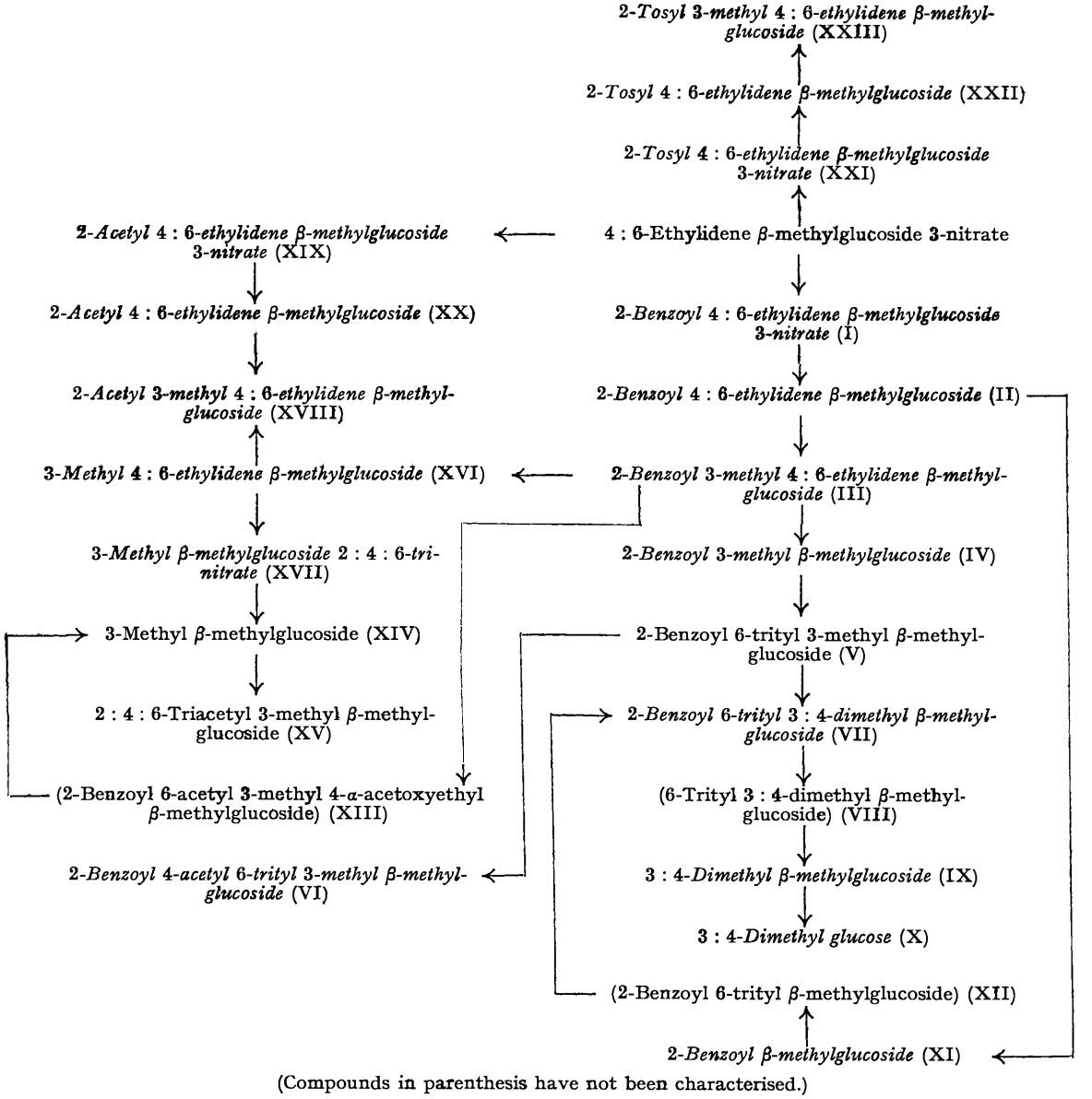
## EXPERIMENTAL.

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

2-*Benzoyl* 4 : 6-*Ethylidene* β-*Methylglucoside* 3-*Nitrate* (I).—Benzoyl chloride (7·9 c.c.) was added gradually to an ice-cold solution of 6 g. of 4 : 6-ethylidene β-methylglucoside 3-nitrate (preceding paper) in dry pyridine. After 4 days at room temperature, the mixture was poured into cold water (400 c.c.), and, after the supernatant liquid had been decanted, the remaining syrup was washed with water and then dissolved in benzene. This solution was washed successively with sulphuric acid (2%), sodium hydroxide (2%), and water, and, after being dried (sodium sulphate) and decolorised (norit), the solvent was removed by distillation. The residual red-brown glass crystallised on treatment with methyl

alcohol, and after recrystallisation (methyl alcohol) yielded plates (7·05 g.), m. p. 123—124°, $[\alpha]_D^{19°}$ +19·9° (chloroform, $l = 2$, $c = 4·789$) (Found: C, 52·5; H, 5·2; N, 3·9; OMe, 8·4. $C_{16}H_{19}O_8N$ requires C, 52·0; H, 5·2; N, 3·8, OMe, 8·4%).

2-*Benzoyl* 4 : 6-*Ethylidene* β-*Methylglucoside* (II).—The above *compound* (1·872 g.) in glacial acetic acid (20 c.c.) was treated with a mixture of iron and zinc powders, the system being kept cold by immersion in water. In 15 minutes the reaction was complete (diphenylamine test) and the mixture was filtered, the residue well washed with chloroform, and the washings added to the filtrate. This chloroform–acetic acid solution was shaken with water, and the aqueous layer extracted with chloroform. After the combined chloroform extracts had been dried (sodium sulphate and potassium carbonate), the solvent was removed by distillation, yielding a crystalline product (1·597 g.). Recrystallisation




(Compounds in parenthesis have not been characterised.)

from ethyl alcohol–light petroleum gave plates, m. p. 190—191°, $[\alpha]_D^{19°}$ −39·5° (chloroform, $l = 2$, $c = 4·927$) (Found: C, 59·4; H, 6·2; OMe, 9·6. $C_{16}H_{20}O_7$ requires C, 59·3; H, 6·2; OMe, 9·6%).

2-*Benzoyl* 3-*Methyl* 4 : 6-*Ethylidene* β-*Methylglucoside* (III).—The above *compound* (II) (1·004 g.) in dry acetone (5 c.c.) after one treatment for 4 hours with methyl iodide (10 c.c.) and silver oxide (10 g.) showed the theoretical increase in weight, and removal of the solvent by distillation yielded crystals, which after recrystallisation (ethyl alcohol–light petroleum) gave plates (0·726 g.), m. p. 159°, $[\alpha]_D^{19°}$ −2·1° (chloroform, $l = 2$, $c = 3·888$) (Found: C, 60·4; H, 6·5; OMe, 18·4. $C_{17}H_{22}O_7$ requires C, 60·4; H, 6·5; OMe, 18·4%).

2-*Benzoyl* 3-*Methyl* β-*Methylglucoside* (IV).—Hydrolysis of the foregoing *compound* (III) was effected by the use of 1% hydrogen chloride in aqueous 75% (v/v) ethyl alcohol. A solution of the compound (0·416 g.) in the acid mixture (25 c.c.) was heated under reflux, the reaction being followed polarimetrically. The rotation changed from an initial negative to a constant positive value (7 hours), at which point excess of calcium carbonate was added, and the solution

filtered. Most of the alcohol was removed by distillation, and the aqueous solution was diluted with water and extracted with benzene, the extract being washed with water. The combined aqueous solution, after addition of sodium chloride, was extracted 6 times with chloroform, and evaporation of the dried (sodium sulphate), combined extracts gave a crystalline residue (0·331 g.). Recrystallisation (ethyl alcohol–light petroleum) gave needles, m. p. 142—143°, $[\alpha]_D^{14°}$ +5·1° (ethyl alcohol, $l = 2$, $c = 1·876$), $[\alpha]_D^{14°}$ +15·2° (acetone, $l = 2$, $c = 5·468$) (Found: C, 57·6; H, 6·5; OMe, 19·4. $C_{15}H_{20}O_7$ requires C, 57·7; H, 6·4; OMe, 19·9%).

2-*Benzoyl* 6-*Trityl* 3-*Methyl* β-*Methylglucoside* (V).—The above *compound* (IV) (0·445 g.) was heated with trityl chloride (0·386 g.; *i.e.*, 97% of the theoretical amount) in pyridine (5 c.c.; dried over phosphoric oxide) for 2 hours in a tightly-stoppered flask on a boiling water-bath. The gum which separated on pouring into water was dissolved in benzene, and the resulting solution was washed in turn with water, dilute sulphuric acid, dilute sodium hydroxide, and water. After drying (sodium sulphate) and removal of solvent by distillation, a yellow glass (0·625 g.) which could not be crystallised was obtained. It showed $[\alpha]_D^{13°}$ −8·9° (chloroform, $l = 2$, $c = 3·03$).

2-*Benzoyl* 4-*Acetyl* 6-*Trityl* 3-*Methyl* β-*Methylglucoside* (VI).—Acetylation of the compound (V) (0·603 g.) with acetic anhydride (0·2 c.c.) in pyridine yielded silky needles (0·605 g.; from ethyl alcohol), m. p. 175°, $[\alpha]_D^{14°}$ +32·0° (chloroform, $l = 2$, $c = 2·092$) (Found: C, 72·6; H, 6·2; OMe, 10·2. $C_{37}H_{38}O_8$ requires C, 72·8; H, 6·2; OMe, 10·2%).

2-*Benzoyl* 6-*Trityl* 3 : 4-*Dimethyl* β-*Methylglucoside* (VII).—(*a*) One treatment (4 hours) with methyl iodide (10 c.c.) and silver oxide (10 g.) sufficed to methylate (V) (1·818 g.). Recrystallisation from methyl alcohol gave needles (67% yield), m. p. 142°, $[\alpha]_D^{14°}$ +36·4° (chloroform, $l = 2$, $c = 4·376$) (Found: C, 73·9; H, 6·5; OMe, 16·3. $C_{35}H_{36}O_7$ requires C, 73·9; H, 6·3; OMe, 16·4%).

(*b*) Methylation of (XII) (0·76 g.) with methyl iodide (10 c.c.) and silver oxide (7 g.) gave, after one treatment, a crystalline product (from methyl alcohol), m. p. 141—142° undepressed on admixture with the product in (*a*).

6-*Trityl* 3 : 4-*Dimethyl* β-*Methylglucoside* (VIII).—The benzoyl compound (VII) (1·975 g.) in absolute methyl alcohol (30 c.c.) was treated with sodium methoxide (0·2 g. of sodium in 5 c.c. of absolute methyl alcohol) at 100° for a few minutes; water was then added, and the solution concentrated by distillation until free from methyl benzoate. On evaporating to dryness a chloroform extract of the residue, a non-crystallisable glass (0·787 g.) was obtained; $[\alpha]_D^{15°}$ +14·2° (chloroform, $l = 2$, $c = 3·765$).

3 : 4-*Dimethyl* β-*Methylglucoside* (IX).—The trityl compound (VIII) (0·733 g.) in dry benzene (15 c.c.) ($\alpha_D$ +0·46° in a 2-dm. tube) was treated with dry hydrogen chloride for 30 minutes (constant $\alpha_D$ −0·24°). The reaction mixture was shaken with water containing sodium acetate and thereafter the aqueous layer was extracted twice with benzene (to complete the removal of tritylcarbinol). Sufficient potassium carbonate was dissolved in the aqueous solution to make this only slightly less dense than chloroform, with which the aqueous solution was extracted 12 times. Removal of the solvent by distillation from the combined extracts gave a syrup (0·334 g.) free from trityl compounds (sulphuric acid test). Further purification was effected by dissolving the syrup in water, extracting the solution 3 times with chloroform, and evaporating it to dryness; the crystalline residue weighed 0·294 g. (82% yield). In subsequent larger-scale preparations, the latter purification was omitted and the crude product was distilled (b. p. 165—169°/0·8 mm.) to yield crystals, which, after recrystallisation from acetone or carbon tetrachloride, had m. p. 79—81°, $[\alpha]_D^{15°}$ −10·9° (acetone, $l = 2$, $c = 5·3820$), −9·3° (ethyl alcohol, $l = 2$, $c = 5·2520$), −11·9° (chloroform, $l = 2$, $c = 5·3751$) (Found: C, 48·8; H, 8·2; OMe, 41·2. $C_8H_{18}O_6$ requires C, 48·7; H, 8·1; OMe, 41·8%).

3 : 4-*Dimethyl Glucose* (X).—The *glucoside* (IX) (0·64 g.) was treated with 2N-hydrochloric acid on a boiling water-bath until a constant rotation was observed (4 hours). An excess of lead carbonate was added, and, after filtration, the solvent was removed by evaporation. The residue was extracted several times with boiling ethyl alcohol, and the combined solutions taken to dryness. Extraction of the residual syrup with hot ethyl acetate and subsequent evaporation gave a crystalline residue (0·55 g.) which readily reduced Fehling's solution; it was further purified by recrystallisation from propyl acetate; m. p. 113°; $[\alpha]_D^{16°}$ +94·5° (8 mins.), $[\alpha]_D^{17°}$ +99·5° (48 hours) (ethyl alcohol, $l = 1$, $c = 2·04$); $[\alpha]_D^{16°}$ +88·5° (6 mins.), $[\alpha]_D^{17°}$ +102·2° (24 hours) (methyl alcohol, $l = 1$, $c = 1·984$); $[\alpha]_D^{18°}$ +64·9° (10 mins.), +94·8° (24 hours) (water, $l = 1$, $c = 0·971$) (Found: C, 46·5; H, 7·5; OMe, 29·1. $C_8H_{14}O_6$ requires C, 46·2; H, 7·7; OMe, 29·8%).

2-*Benzoyl* β-*Methylglucoside* (XI).—A solution of the compound (II) (1·614 g.) in aqueous 75% ethyl alcohol (30 c.c.) containing 1% hydrochloric acid was heated in the manner described for the conversion of (III) into (IV), a constant rotation being observed after 3 hours. After neutralisation with calcium carbonate, filtration, and evaporation to dryness, the residue was extracted with hot acetone–chloroform (2 : 1); evaporation of this solution gave crystals (1·378 g.), from which (*ex* alcohol–light petroleum) needles were obtained, m. p. 174—177°, $[\alpha]_D^{13°}$ −1·8° (acetone, $l = 4$, $c = 1·77$) (Found: C, 56·5; H, 6·1; OMe, 10·6. $C_{14}H_{18}O_7$ requires C, 56·4; H, 6·0; OMe, 10·4%).

2-*Benzoyl* 6-*Trityl* β-*Methylglucoside* (XII).—Treatment of the above *compound* (XI) (0·51 g.) with trityl chloride 0·453 g.; 95% of the theoretical amount) in pyridine (5 c.c.), as described for the compound (V), gave a colourless glass ((0·765 g.), $[\alpha]_D^{12°}$ −25·8° (chloroform, $l = 2$, $c = 3·8$).

2-*Benzoyl* 6-*Acetyl* 3-*Methyl* 4-α-*Acetoxyethyl* β-*Methylglucoside* (XIII).—After the rotation (−0·170°) of a solution of pure (III) (0·512 g.) in acetic anhydride (10 c.c.) had been observed, a drop of concentrated sulphuric acid was added and the course of the reaction followed polarimetrically (cf. Bell and Synge, *loc. cit.*). When a constant value (+2·98°) was reached (30 mins.), the solution was poured into water (70 c.c.) containing a little sodium acetate and shaken. The solution was then extracted with benzene, the benzene layer washed with potassium hydrogen carbonate solution, and the dried (sodium sulphate) solution evaporated to dryness; it gave a colourless syrup (0·596 g.) which did not crystallise.

3-*Methyl* β-*Methylglucoside* (XIV).—(*a*) The compound (XIII) (0·548 g.) in absolute methyl alcohol (5 c.c.) was heated on a water-bath with a solution of sodium (0·092 g.) in methyl alcohol (5 c.c.) for 5 minutes, the calculated amount (0·230 c.c.) of glacial acetic acid and water (10 c.c.) added, and the solution concentrated by distillation to remove all the methyl alcohol and methyl benzoate. The residual aqueous solution was shaken 3 times with chloroform (to remove unchanged material), decolourised (norit), and evaporated to dryness. Extraction with hot acetone and subsequent evaporation of the filtered extract gave a syrup (0·243 g.), $[\alpha]_D^{14°}$ −25·3° (water, $l = 2$, $c = 1·59$) (Found: OMe, 13·5. Calc. for $C_8H_{16}O_6$: OMe, 13·4%). Helferich and Lang (*J. pr. Chem.*, 1932, **132**, 321) give $[\alpha]_D^{20°}$ −26·9° (water).

(*b*) A sample of (XVII) (0·629 g.) in glacial acetic acid (7 c.c.) was reduced by an excess of zinc and iron powders, the reaction vessel being heated over a free flame. Cessation of the evolution of brown fumes indicated the completion of the reaction, and the absence of nitrate was confirmed by the diphenylbenzidine test. The reaction mixture was then poured into water–acetone (1 : 4) containing calcium carbonate; after being stirred until the evolution of carbon dioxide ceased, the solution was filtered and evaporated to dryness. The residue was extracted with acetone, and, after filtering, the solvent was distilled off, leaving a syrup (0·226 g.). Further purification was effected as in (*a*), and the resultant syrup (0·159 g.) was identical in its characteristics with the product in (*a*) and gave the same triacetate (see below).

2 : 4 : 6-*Triacetyl* 3-*Methyl* β-*Methylglucoside* (XV).—Treatment of (XIV) (0·221 g.) with acetic anhydride (0·6 c.c.) in pyridine (6 c.c.) gave a crystalline product (0·344 g.) forming, from light petroleum–ethyl alcohol, needles, m. p. 91·5°; $[\alpha]_D^{14°}$ −36·4° (chloroform, $l = 2$, $c = 1·856$) (Found: C, 50·3; H, 6·6; OMe, 18·2. Calc. for $C_{14}H_{22}O_9$: C, 50·3; H, 6·6; OMe, 18·5%). Helferich and Lang (*loc. cit.*) give m. p. 90—90·5°, $[\alpha]_D^{20°}$ −34·8° (chloroform).

3-*Methyl* 4 : 6-*Ethylidene* β-*Methylglucoside* (XVI).—The compound (III) (1·01 g.) in absolute methyl alcohol (30 c.c.) was treated with sodium methoxide (0·2 g. of sodium in 5 c.c. of absolute methyl alcohol) on a boiling water-bath for a few minutes: water was then added, and the solution concentrated by distillation until free from methyl benzoate. The aqueous residue was diluted with water and then shaken 4 times with chloroform; the chloroform solution was dried (sodium sulphate) and evaporated, giving a crystalline product (0·661 g.); needles (*ex* light petroleum–ethyl alcohol), m. p. 134°; $[\alpha]_D^{19°}$ −43·7° (chloroform, $l = 2$, $c = 4·642$) (Found: C, 51·3; H, 7·6; OMe, 26·2 $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7; OMe, 26·5%).

3-*Methyl* β-*Methylglucoside* 2 : 4 : 6-*Trinitrate* (XVII).—To an ice-cold solution of (XVI) (0·638 g.) in chloroform (15 c.c.) was added a cold mixture of fuming nitric acid (20 c.c.) and chloroform (20 c.c.); after 15 minutes at 0° the mixture was poured into ice and water and shaken rapidly. The chloroform solution was then washed with sodium hydrogen carbonate solution, dried with sodium sulphate, and evaporated. The resultant syrup (0·856 g.) crystallised rapidly; recrystallised from methyl alcohol, it formed needles, m. p. 56—57°, $[\alpha]_D^{14°}$ −1·6° (chloroform, $l = 2$, $c = 1·841$). The *nitrate* was mildly explosive above its m. p. (Found: C, 28·7; H, 3·8; N, 12·1; OMe, 18·1. $C_8H_{13}O_{12}N_3$ requires C, 28·0; H, 3·8; N, 12·3; OMe, 18·1%).

2-*Acetyl* 3-*Methyl* 4 : 6-*Ethylidene* β-*Methylglucoside* (XVIII).—(*a*) The compound (XVI) (0·678 g.) was acetylated by treatment with acetic anhydride (0·413 c.c.) in anhydrous pyridine (10 c.c.) for 2 days at room temperature. Isolation by extraction with chloroform, the extract being washed in the usual manner, gave, on distillation of the solvent, a crystalline residue (0·811 g.), m. p. 101—103° (*ex* light petroleum), $[\alpha]_D^{17°}$ −41·2° (chloroform, $l = 2$, $c = 2·831$) (Found: C, 52·3; H, 6·8; OMe, 22·5. $C_{12}H_{20}O_7$ requires C, 52·1; H, 7·2; OMe, 22·5%).

(*b*) One methylation by Purdie's method of a sample of (XX) (0·516 g.) gave a syrup (0·52 g.), which crystallised immediately on nucleation with the product obtained as in (*a*). After recrystallisation as in (*a*), the m. p. was 101—103°, unaltered on mixing with a sample from (*a*) but depressed by 3-acetyl 2-methyl 4 : 6-ethylidene β-methylglucoside (m. p. 113°; preceding paper).

2-*Acetyl* 4 : 6-*Ethylidene* β-*Methylglucoside* 3-*Nitrate* (XIX).—4 : 6-Ethylidene β-methylglucoside 3-nitrate (2 g.) in pyridine was treated with acetic anhydride (1·05 c.c.) for 24 hours at room temperature. Isolation in the usual way by means of benzene gave a crystalline product (2·26 g.), m. p. 129—130°, $[\alpha]_D^{21°}$ −44·8° (chloroform, $l = 2$, $c = 5·2$) (Found: C, 43·0; H, 5·4; N, 4·9; OMe, 10·1. $C_{11}H_{17}O_8N$ requires C, 43·0; H, 5·6; N, 4·6; OMe, 10·1%).

2-*Acetyl* 4 : 6-*Ethylidene* β-*Methylglucoside* (XX).—(*a*) A solution of (XIX) (1·915 g.) in acetone (40 c.c.) and water (1 c.c.) was shaken mechanically with liquid zinc amalgam for 5 hours (negative test for nitrate with diphenylbenzidine) and then filtered. On removal of solvent by evaporation, a glass (1·802 g.) was obtained; this was dissolved in chloroform, and the solution washed several times with water. After drying (sodium sulphate), the chloroform was distilled off, giving a glass (1·04 g.) which did not crystallise; $[\alpha]_D^{15°}$ −52·8° (chloroform, $l = 2$, $c = 3·196$) (Found: OMe, 11·9; Ac, 16·4. $C_{11}H_{18}O_7$ requires OMe, 11·8; Ac, 16·4%).

(*b*) The same product with identical characteristics was also obtained by reducing a sample of (XIX) (0·863 g.) in glacial acetic acid (15 c.c.) with equal parts of zinc and iron powders. The yield (0·705 g.) was 96%, in contrast to 64% from (*a*).

2-*Tosyl* 4 : 6-*Ethylidene* β-*Methylglucoside* 3-*Nitrate* (XXI).—A 50% excess of *p*-toluenesulphonyl chloride (5·02 g.) was added to a solution of 4 : 6-ethylidene β-methylglucoside 3-nitrate (4·66 g.) in dry pyridine (16 c.c.), and, after shaking, the mixture was left at room temperature for 6 days. Isolation in the standard manner gave crystals (6·195 g.), m. p. 136—139°. The pure *substance*, m. p. 143—144°, $[\alpha]_D^{19°}$ −10·3° (chloroform, $l = 2$, $c = 5·429$), was obtained by recrystallisation from methyl alcohol (Found: C, 45·9; H, 5·1; N, 3·5; OMe, 7·4. $C_{16}H_{21}O_{10}NS$ requires C, 45·8; H, 5·1; N, 3·3; OMe, 7·4%).

2-*Tosyl* 4 : 6-*Ethylidene* β-*Methylglucoside* (XXII).—A warm solution of this nitrate (6·205 g.) in glacial acetic acid (50 c.c.) was treated with zinc and iron powders for 10 minutes and the product isolated as before (I → II). The resultant syrup (5·45 g., $n_D$ 1·5140) crystallised on standing, and the pure material (plates, *ex* light petroleum–ethyl alcohol) had m. p. 152—153°, $[\alpha]_D^{18°}$ −45·5° (chloroform, $l = 2$, $c = 3·385$) (Found: C, 51·7; H, 5·8; OMe, 8·2. $C_{16}H_{22}O_8S$ requires C, 51·3; H, 5·9; OMe, 8·3%).

2-*Tosyl* 3-*Methyl* 4 : 6-*Ethylidene* β-*Methylglucoside* (XXIII).—Treatment of (XXII) (1·001 g.) in acetone (5 c.c.) with methyl iodide (10 c.c.) and silver oxide (10 g.) for 4 hours gave a syrup (theoretical yield) which crystallised in contact with methyl alcohol. The pure *substance* (*ex* light petroleum–ethyl alcohol) had m. p. 123—124°, $[\alpha]_D^{20°}$ −22·8° (chloroform, $l = 2$, $c = 3·885$) (Found: C, 52·3; H, 6·0; OMe, 15·5. $C_{17}H_{24}O_8S$ requires C, 52·6; H, 6·2; OMe, 16·0%).

*Acetolysis of* 2-*Methyl* 4 : 6-*Ethylidene* β-*Methylglucoside* 3-*Nitrate* [Bell and Synge (*loc. cit.*); Dewar and Fort (*loc. cit.*)].—The nitrate (2·5 g.) was dissolved in acetic anhydride (50 c.c.), concentrated sulphuric acid (0·05 c.c.) added, and the course of the reaction followed polarimetrically [$\alpha_D$ (5 mins.) + 0·92° ($l = 2$)]. After 50 mins. [($\alpha_D$ +3·47° ($l = 2$)], the solution was shaken with ice-water (250 c.c.) containing some sodium acetate. The whole was then extracted 3 times with benzene, and the extract washed with sodium hydrogen carbonate solution, dried (sodium sulphate), and evaporated, giving a syrup (3·4 g.; $n_D^{16°}$ 1·4590) (Found: OMe, 15·2. Calc. for 6-acetyl 2-methyl 4-α-acetoxyethyl β-methylglucoside 3-nitrate, $C_{14}H_{23}O_{11}N$: OMe, 16·3%). Attempts to crystallise freshly prepared material failed, but, after several months, crystals were formed; m. p. 130—132° (*ex* methyl alcohol), $[\alpha]_D^{16°}$ −47·0° (chloroform, $l = 2$, $c = 1·8$) (Found: C, 40·8; H, 5·8; N, 4·7; OMe 20·8. Calc. for a monoacetyl monomethyl methylglucoside mononitrate, $C_{10}H_{17}O_8N$: C, 40·7; H, 5·8; N, 4·7; OMe, 21·0%). Freshly prepared syrup could not be induced to crystallise by nucleation with this crystalline product.

The authors acknowledge their indebtedness to the Carnegie Trust for the grant of a Scholarship which enabled one of them (G. F.) to take part in this and the preceding investigation, and to Dr. J. W. H. Oldham (Royal Institution) for his interest and kindly criticism.

THE UNIVERSITY, ST. ANDREWS. [*Received, June 13th*, 1944.]