38. *The Simultaneous Formation of Two Isomeric* iso*Propylidene Derivatives of 2-Methyl* γ*-Methylglucoside.*

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RECENT experiments in this laboratory demanded that the position of the hydroxyl groups involved in the condensation with acetone of 2-methyl γ-methylglucoside should be determined. Macdonald (J., 1913, **103**, 1896) and Irvine, Fyffe, and Hogg (J., 1915, **107**, 524) concluded from the evidence then available that *iso*propylidene γ-methylglucoside had free hydroxyls in positions 2 and 3. The discovery of *iso*diacetoneglucose (1 : 2 : 3 : 5) by Freudenberg *et al.* (*Ber.*, 1928, **61**, 1735) and of 3 : 5-benzylidene *iso*propylidene glucose by Brigl and Grüner (*Ber.*, 1932, **65**, 1428), coupled with the spatial position in glucofuranose of hydroxyl groups 3 and 5, rendered not impossible a configuration alternative to that suggested by the original workers in this field. As detailed below, the present author finds that condensation between acetone and 2-methyl γ-methylglucoside, catalysed by 1% sulphuric acid and anhydrous copper sulphate, leads to the formation of a mixture of 3 : 5- and 5 : 6-iso*propylidene* derivatives.

The steps in the investigation may be summarised as follows : (1) Condensation of acetone with the glucoside, (2) methylation of vacant hydroxyl groups, (3) hydrolysis of glucosidic methyl and *iso*propylidene groups, (4) conversion of free sugars into β-glucosides, (5) isolation of crystalline 2 : 3-dimethyl β-methylglucoside 4 : 6-dinitrate, (6) isolation of crystalline 3 : 4-di-*p*-toluenesulphonyl 2 : 6-dimethyl β-methylglucoside. No attempt was made to conduct a quantitative examination of the relative amounts of the two *iso*propylidene isomerides.

EXPERIMENTAL.

Condensation of Acetone and 2-Methyl γ*-Methylglucoside.*—To 13 g. of the glucoside (Oldham and Rutherford, *J. Amer. Chem. Soc.*, 1932, **54**, 1086), dissolved in 150 ml. of acetone, 25 g. of anhydrous copper sulphate and 1·5 ml. of concentrated sulphuric acid were added and the whole was kept at room temperature for 18 hours. After filtration to remove inorganic material, the acetone was distilled off under reduced pressure, in the presence of a little sodium carbonate. The residue was dissolved in water, filtered through norit, and extracted six times with chloroform. The extract, after dehydration, was evaporated to dryness in a vacuum, 11·5 g. of a colourless, fairly mobile syrup being obtained (Found : OMe, 25·4. $C_{11}H_{20}O_6$ requires OMe, 25·4%).

Methylation of the product. 11 G. were twice methylated with Purdie's reagents, a very mobile, colourless syrup (11 g.) having the composition of a trimethyl *iso*propylidene hexose being obtained (Found : OMe, 35·4. $C_{12}H_{22}O_6$ requires OMe, 35·5%).

Aqueous-acid hydrolysis. 10 G. of the above product were hydrolysed by heating at 100° in 100 ml. of 0·5% hydrochloric acid until constant polarimetric readings were obtained (180 mins.). After neutralisation with silver carbonate and extraction of the crude product with ethyl acetate, 7·0 g. (84%) of dimethylated sugars were obtained as a colourless glass.

Conversion into β-glucosides. This was effected by the procedure of Oldham (*J. Amer. Chem. Soc.*, 1934, **56**, 1360). The crude yield was 4·0 g., but after 4 hours' boiling with *N*/70-hydrochloric acid to eliminate furanosides, the yield fell to 3·25 g.

Isolation of 2 : 3*-Dimethyl β-Methylglucoside* 4 : 6*-Dinitrate.*—2 G. of the crude dimethyl methylglucoside were converted into the dinitric ester as described by Oldham and Rutherford (*J. Amer. Chem. Soc.*, 1932, **54**, 366). The product was a mixture of syrup and crystals (yield, 0·7 g.), m. p. 99—100°, $[\alpha]_D^{20^\circ}$ − 20·8° (in chloroform ; $l = 2$, $c = 4{\cdot}0$). Oldham and Rutherford record for 2 : 3-dimethyl β-methylglucoside 4 : 6-dinitrate, m. p. 98—99° and $[\alpha]_D$ − 20·8°. The m. p. of a mixture of a specimen of this substance with the product described above showed no depression (Found : OMe, 29·9. Calc. for $C_9H_{16}O_{10}N_2$: OMe, 29·9%).

Isolation of 3 : 4*-Di-*p*-toluenesulphonyl* 2 : 6*-Dimethyl β-Methylglucoside.*—The syrupy portion (1·7 g.) of the crude dinitrate was denitrated with zinc and iron in acetic acid. After appropriate isolation, the resulting glucoside (1·0 g.) showed $[\alpha]_D^{20^\circ}$ − 22° (in chloroform) (2 : 3-dimethyl β-methylglucoside has $[\alpha]_D$ − 45°; Oldham, *loc. cit.*). It was converted into the ditoluenesulphonate in the usual way, a crystalline product being obtained ; the m. p., however, indicated that it was a mixture. 1·91 G. were treated by the processes described by Oldham and Rutherford (*J. Amer. Chem. Soc.*, 1932, **54**, 366) by which a nitro-group is substituted for a toluenesulphonyl group in position 6; any 2 : 3-dimethyl derivative present was thus rendered more soluble. On treatment of the crude product with ether, crystals separated. These, on recrystallisation from alcohol containing 10% of acetone, yielded 0·5 g. of needles, m. p. 157—159°, $[\alpha]_D^{20°}$ − 8·9° (in chloroform; $l = 2$, $c = 3·0$). A mixed m. p. determination with 3 : 4-ditoluenesulphonyl 2 : 6-dimethyl β-methylglucoside ($[\alpha]_D$ − 8·8°; Oldham and Rutherford) showed no depression (Found : OMe, 17·4. Calc. for $C_{23}H_{30}O_{10}S_2$: OMe, 17·5%).

The author is indebted to the Commissioners for the Exhibition of 1851 for the award of a Senior Studentship and to the Medical Research Council for a grant.

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