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## Note

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# Selective deacetylation of sucrose octa-acetate with primary amines to give 2,3,4,6,1′,6′-hexa-*O*-acetylsucrose*

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The selective removal of protecting groups in carbohydrate derivatives provides a useful route to partially protected compounds[1]. This type of approach is attractive for the chemical modification of sucrose, and the selective deacetylation of sucrose octa-acetate (**1**) has been studied in chloroform solution on aluminium oxide[2,3] and in methanol solution on aluminium oxide impregnated with potassium carbonate[4,5]. We now report on the selective deacetylation that occurs when **1** is dissolved in propylamine or isopropylamine, in which the ester is readily soluble.

On storage of a 0.15M solution of **1** in propylamine at ambient temperature, the octa-acetate gradually disappeared during ~50 min (t.l.c., ethyl acetate–ether). The products had lower mobility and, after ~85 min, only material that remained on the base line was present. Between 35 and 45 min, four components were detected with mobilities between that of **1** and the base-line material but, at 50 min, only the two least mobile of these components were apparent. Evaporation of the solvent (b.p. 48°) at this time and column chromatography of the residue on silica gel gave the major component as a syrup which showed i.r. absorptions for hydroxyl and carbonyl groups and which analysed for a hexa-acetate. The structure of the product was determined using the Rathbone method[6] (acetylation with acetic anhydride-$d_6$ and measurement of the $^1$H-n.m.r. spectrum of the product in benzene-$d_6$–pyridine-$d_5$). Six signals for AcO groups were observed with chemical shifts corresponding to the 2,3,4,6,1′,6′-positions. Therefore, the partially *O*-deacetylated compound (22% yield) was 2,3,4,6,1′,6′-hexa-*O*-acetylsucrose (**2**), indicating the secondary positions in the furanose ring to be the sites most reactive towards deacetylation by the amine. A similar selectivity was observed in studies of the deacetylation of **1** with aluminium oxide impregnated with

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* Dedicated to Professor Leslie Hough in the year of his 65th birthday.

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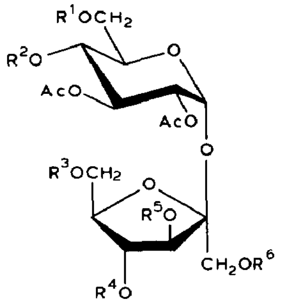

**1** $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = Ac$
**2** $R^1 = R^2 = R^3 = R^6 = Ac, R^4 = R^5 = H$
**3** $R^1 = R^4 = R^5 = Ac, R^2 = R^3 = R^6 = CD_3CO$
**4** $R^1 = R^4 = R^5 = Ac, R^2 = R^3 = R^6 = H$

potassium carbonate[4], which afforded a mixture of **2** and the 2,3,4,6,4′,6′-hexa-acetate with the former preponderating. Our synthesis provides the first direct preparation of **2**.

The preferential removal of acetyl residues from secondary rather than primary positions invites speculation that cleavage might occur selectively at the primary 1′,6′-positions followed by acyl migration from the 3′,4′-positions[3]. That this does not occur was shown by aminolysis of 2,3,6,3′,4′-penta-*O*-acetyl-4,1′,6′-tri-*O*-trideuterioacetylsucrose (**3**), readily prepared from the known[7] 2,3,6,3′,4′-penta-*O*-acetylsucrose (**4**). Treatment of **3** with propylamine, as for **1**, afforded, after chromatography, a syrup which was acetylated with acetic anhydride–pyridine to give a product that was chromatographically indistinguishable from **1** and **3**. Application of the Rathbone method[6] indicated acetyl groups only at the 2,3,6,3′,4′-positions. It is pertinent that there was no 4′→6′ or 6′→4′ acetyl migration during deacetylation of the 2,3,4,6,1′,3′,4′- and 2,3,4,6,1′,3′,6′-hepta-acetates, respectively, to hexa-acetates with aluminium oxide–potassium carbonate in methanol[5].

Deacetylation of **1** in isopropylamine occurred much more slowly than in propylamine. Only after 72 h was the composition of the mixture similar to that reached after 50 min with propylamine. Isolation of the main component by column chromatography afforded **2** (15%).

T.l.c. of solutions of **1** in *tert*-butylamine, which had been purified by distillation from the octa-acetate, gave little indication of deacetylation after 5 days, and only on prolonged storage was a small proportion of material detected that appeared, from its chromatographic mobility, to be a hepta-acetate.

Treatment of a solution of **1** in dichloromethane with 3 mol of either propylamine or isopropylamine at room temperature, or under reflux, brought about no deacetylation.

## EXPERIMENTAL

The $^1$H- and $^{13}$C-n.m.r. spectra (internal $Me_4Si$, unless stated otherwise) were recorded at 399.65 and 100.4 MHz, respectively, with a JEOL GX400 spectrometer. The chemical shifts of the AcO resonances in sucrose octa-acetate and in the labelled sucrose octa-acetates were measured[6] for 2% solutions in $C_6D_6$–$C_5D_5N$ (1:1) with residual benzene ($\delta$ 7.150) as the reference. T.l.c. was performed on silica gel, using ethyl acetate–ether (1:1). Column chromatography was performed on silica gel (Merck, 70–230 mesh).

*Selective deacetylation of sucrose octa-acetate* (**1**). — (*a*) *In propylamine.* A solution of **1** (2.0 g) in propylamine (20 mL) was stored at room temperature for 50 min and then concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (130 g) with ethyl acetate–ether (7:4), and the fractions containing the major component ($R_F$ 0.3) were combined and concentrated to give syrupy 2,3,4,6,1′,6′-hexa-*O*-acetylsucrose (**2**; 0.382 g, 22%), $[\alpha]_D$ +65° (*c* 0.77, chloroform), $\nu_{max}$ 3700–3200 (OH) and 1740 cm$^{-1}$ (C=O). N.m.r. data ($CDCl_3$): $^1$H, $\delta$ 2.02, 2.04, 2.08, 2.11 ( × 2), 2.13 (6 s, 6 AcO), 2.33, 3.50 (2 s, 2 OH), 4.12–4.33 (complex, 10 H, H-5,6a,6b,1′a,1′b,3′,4′,5′,6′a,6′b), 4.93 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 10.0 Hz, H-2), 5.04 (t, 1 H, $J_{3,4} = J_{4,5}$ = 10 Hz, H-4), 5.46 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10 Hz, H-3), 5.64 (d, 1 H, H-1); $^{13}$C, $\delta$ 20.61, 20.74 ($CH_3CO$), 60.5, 62.2, 63.4, 64.0, 68.3, 68.6, 69.8, 70.1, 74.8, 77.7, 79.1, 103.1 (C-1/C-6 and C-1′/C-6′), 169.6, 170.0, 170.5*, 171.0, 171.4 (6 $CH_3CO$) (*enhanced intensity).

*Anal.* Calc. for $C_{24}H_{34}O_{17}$: C, 48.5; H, 5.8. Found: C, 48.3; H, 5.85.

(*b*) *In isopropylamine.* A solution of **1** (0.5 g) in isopropylamine (10 mL) was stored at room temperature for 72 h. Column chromatography [ethyl acetate–ether (7:4)] of the residue obtained on concentration of the mixture gave 2,3,4,6,1′,6′-hexa-*O*-acetylsucrose (**2**) as the major component (0.061 g), $R_F$ 0.3.

*Determination of the structure of the partially acetylated sucrose.* — The method is essentially that of Rathbone[6]. To a portion (0.02 g) of the partially acetylated sucrose was added pyridine (1 mL) followed by acetic anhydride-$d_6$ (0.5 mL), and the solution was stored at room temperature for 24 h. Water (1 mL) was added, the mixture was shaken for 15 min, the supernatant liquid was removed, and the residue was washed with water at 0°, then dried under reduced pressure over $P_2O_5$ for 24 h. The product was dissolved in 1:1 benzene-$d_6$–pyridine-$d_5$ to afford a ~2% solution, and the $^1$H-n.m.r. spectrum was measured with residual benzene ($\delta$ 7.150) as the reference. In the region $\delta$ 1.700–2.000, six peaks of equal intensity were observed at $\delta$ 1.758, 1.783, 1.807, 1.831, 1.885, and 1.898 that corresponded to acetyl groups at the 4,3,1′,6′,6,2-positions, respectively; resonances for AcO-3′,4′ would be expected at $\delta$ ~1.936 and ~1.732*.

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* Under similar conditions, the $^1$H-n.m.r. spectrum of sucrose octa-acetate contained resonances for acetyl groups at $\delta$ 1.936, 1.898, 1.887, 1.829, 1.804, 1.784, 1.757, and 1.732 that correspond to the 3′,2,6,6′,1′,3,4,4′-positions. In the same solvent mixture, with benzene as internal reference, Rathbone obtained[9] the values: $\delta$ 1.937, 1.899, 1.888, 1.829, 1.805, 1.784, 1.757, and 1.732.

*Acyl migration experiments.* — 2,3,6,3′,4′-Penta-*O*-acetyl-4,1′,6′-tri-*O*-trideuterioacetylsucrose (**3**), prepared by conventional acylation of 2,3,6,3′,4′-penta-*O*-acetylsucrose[7] (**4**) with acetic anhydride-$d_6$ in pyridine, had m.p. 86–88° (for octa-*O*-acetylsucrose, lit.[8] m.p. 83.5–87°). $^1$H-N.m.r. data ($C_6D_6$–$C_5D_5N$ 1:1): $\delta$ 1.938, 1.900, 1.888, 1.786, and 1.734 (AcO at the 3′,2,6,3,4′-positions).

A solution of the isotopically labelled octa-acetate (0.81 g) in propylamine (5 mL) was stored at room temperature for 50 min and the major product was isolated as for the unlabelled compound. This material was acetylated with an excess of acetic anhydride in pyridine in the usual manner to give a syrup (0.12 g). $^1$H-N.m.r. data ($C_6D_6$–$C_5D_5N$ 1:1): $\delta$ 1.943, 1.901, 1.886, 1.786, and 1.741 (AcO at the 3′,2,6,3,4′-positions). In order to confirm the allocation of the peaks, a trace of **1** was added to the solution and the $^1$H-n.m.r. spectrum was remeasured; new peaks were observed at $\delta$ 1.832, 1.809, and 1.762 (AcO at the 6′,1′,4-positions).

## ACKNOWLEDGMENT

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