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Note

Selective de-acetalation of 1',2:4,6-di-*O*-isopropylidenesucrose tetra-acetate*

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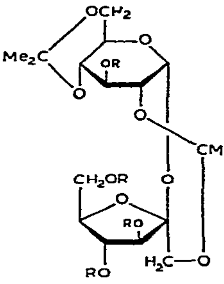
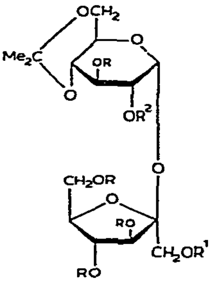
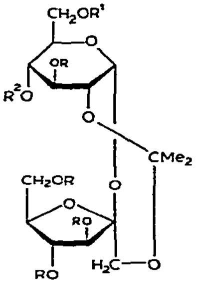
We have described the selective de-esterification of 1',2 4,6-di-*O*-isopropylidenesucrose tetra-acetate[2] (**1**), to give the corresponding 3'- and 4'-mono-, 3',4'-di-, 3',4',6'-tri-, and 3,3',4',6'-tetra-hydroxy derivatives[3] We now report on the selective de-acetalation of **1** by use of aqueous acetic acid, methanolic hydrogen chloride, and cation-exchange resins According to t l c , all three reagents were equally effective However, from a practical point of view, the first reagent is the most convenient Treatment of **1** with aqueous acetic acid at room temperature for 4 h gave, in addition to **1** (11 %), 3,3',4',6'-tetra-*O*-acetyl-4,6-*O*-isopropylidenesucrose (**2**, 4 7 %), 3,3',4',6'-tetra-*O*-acetyl-1',2-*O*-isopropylidenesucrose (**3**, 23 %), and 3,3',4',6'-tetra-*O*-acetylsucrose[2] (**4**, 28 %) On the basis of the yields of the monoacetals **2** and **3**, it is concluded that the eight-membered (1',2) cyclic acetal group in **1** is more stable, under these reaction conditions, than the six-membered (4,6) cyclic acetal group



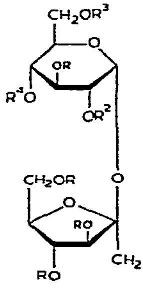
1 R = Ac



2 $R^1 = R^2 = H$ R = Ac
5 $R^1 = R^2 = R = Ac$



3 $R^1 = R^2 = H$ R = Ac
7 $R^1 = R^2 = R = Ac$



4 $R^1 = R^2 = R^3 = R^4 = H$ R = Ac
6 $R^1 = R^2 = Ms, R^3 = R^4 = R = Ac$
8 $R^1 = R^2 = H, R^3 = R^4 = R = Ac$

The structure of **2** was proved by chemical transformations, and by ^{1}H-n m r and mass spectrometry Conventional acetylation of **2**, using acetic anhydride and

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*Sucrochemistry Part XXVI For Part XXV, see Ref 1 pyridine, gave the known[1] 4,6-*O*-isopropylidenesucrose hexa-acetate (**5**) Further proof of the structure of **2** was obtained by its conversion into the known[4] 1′,2-di-*O*-mesylsucrose hexa-acetate (**6**) Treatment of **2** with mesyl chloride in pyridine, followed by de-acetalation with aqueous acetic acid and conventional acetylation, gave the 1′,2-dimesylate **6** in 55% yield

The ^{1}H-n m r spectrum of **3** showed two peaks at τ 8 54 and 8 75 due to the presence of an isopropylidene group The signals due to H-2 (τ 6 27) and H-4 (τ 6 0–6 7) appeared at relatively high field, which indicated that C-2 and C-4 were either involved in cyclic acetal linkage or carried hydroxyl groups Addition of trichloroacetyl isocyanate to the solution of **3** in deuteriochloroform generated, in the ^{1}H-n m r. spectrum, singlets at τ 0 25 and 1 52 due to imino protons, thereby indicating the presence of two hydroxyl groups in **3** Also, the resonance due to H-4 was shifted to τ 5 18, thereby confirming the presence of one of the hydroxyl groups at C-4 This, in turn, suggested that the second hydroxyl group in **3** was located at C-6 The structure of **3** was confirmed by the following chemical transformations Conventional acetylation of **3** with acetic anhydride and pyridine gave the hexa-acetate **7**, the structure of which was supported by its ^{1}H-n m r spectrum The signals due to an isopropylidene group appeared at τ 8 54 and 8 75, and the characteristic high-field quartet due to H-2 at τ 6 16 indicated the presence of the 1′,2-cyclic acetal group in **7** and consequently in **3** Treatment of **7** with 60% aqueous acetic acid for 15 min at 90° gave the known[5] 3,4,6,3′,4′,6′-hexa-*O*-acetylsucrose (**8**) in 61% yield

EXPERIMENTAL

For details of general procedure, see Part XXIV[3]

De-acetalation of 1′,2 4,6-di-O-isopropylidenesucrose tetra-acetate (**1**) — (*a*) A solution of **1** (13 6 g) in acetone (10 ml) was treated with acetic acid–water (2 3) at room temperature for 4 h The reaction mixture was then diluted with dichloromethane and washed thoroughly with aqueous sodium hydrogen carbonate, and the organic layer was dried ($MgSO_4$) and concentrated to give a syrup (6 9 g) The aqueous phase was concentrated, the resulting residue was taken up in dichloromethane, and the solid residue was filtered off The solution was then concentrated to afford a syrup (6 2 g)

The first syrup was eluted from a column of silica gel (500 g) to give, first, 1′,2 4,6-di-*O*-isopropylidenesucrose tetra-acetate (**1**, 1 5 g, 11%), m p and mixture m p 135–137° The ^{1}H-n m r spectrum in deuteriobenzene was identical to that of the authentic sample N m r data ($CDCl_3$) τ 3 92 (d, 1 H, $J_{1,2}$ 3 5 Hz, H-1), 6 20 (q, 1 H, $J_{2\ 3}$ 10 0 Hz, H-2), 4 78 (t, 1 H, $J_{3,4}$ 10 0 Hz, H-3), 6 00–6 42 (H-4), 7 80–8 00 (12 H, 4 Ac), 8 56, 8 58, 8 60, and 8 72 (s, 12 H, 4 Me)

Eluted second was 3,3′,4′,6′-tetra-*O*-acetyl-4,6-*O*-isopropylidenesucrose (**2**, 0 6 g, 4 7%), $[\alpha]_D$ +28° (*c* 0 98, chloroform) N m r. data ($CDCl_3$) τ 4 9 (t, 1 H, $J_{2\ 3}$ 9 0 Hz, H-3), 7 85–9 01 (12 H, 4 Ac), 8 61, and 8 70 (s, 6 H, 2 Me) N m r. data ($CDCl_3$–trichloroacetyl isocyanate) τ 4 24 (d, 1 H, $J_{1,2}$ 3 6, H-1), 5 15 (q, 1 H, $J_{2,3}$ 10 0 Hz, H-2), 4 68 (t, 1 H, $J_{3\,4}$ 10 0 Hz, H-3), 0 85, and 1 12 (s, 2 H, NH) Mass-spectral data [(a) indicates hexopyranosyl and (b) ketofuranosyl cations] *m/e* 289(b), 245(a), 229(b), 187(b), 185(a), 170(a), 169(b), 127(b), 109(b), 101, and 43

Anal Calc for $C_{23}H_{34}O_{15}$ C, 50 2, H, 6 2 Found C, 51 1, H, 6 2

Eluted third was 3,3′,4′,6′-tetra-*O*-acetyl-1′,2-*O*-isopropylidenesucrose (**3**, 2 9 g, 22 8%), $[\alpha]_D$ +18° (*c* 0 94, chloroform) N m r data ($CDCl_3$) τ 3 93 (d, 1 H, $J_{1\,2}$ 3 5 Hz, H-1); 6 28 (q, 1 H, $J_{2\,3}$ 9 0 Hz, H-2), 4 91 (t, 1 H, $J_{3\,4}$ 9 0 Hz, H-3), 7 80–8 00 (12 H, 4 Ac), 8 54, and 8 75 (s, 6 H, 2 Me)

Anal Calc for $C_{23}H_{34}O_{15}$ C, 50 2, H, 6 2 Found C, 50 4, H, 6 3

The second, syrupy residue was eluted from a column of silica gel (200 g) with dichloromethane–methanol (10 1), to give **4** (3 3 g, 28 1%), m p 128–130° (from acetone–ether); lit [2] m p 121–123° The ^{1}H-n m r spectrum of **4** was indistinguishable from that of an authentic sample[2]

(*b*) A solution of **1** (0 2 g) in methanol was heated (70°) with Amberlite IRC-72 (H^+) resin for 24 h T l c (dichloromethane–methanol, 9 0 5) indicated the products **1**–**4** in approximately the same ratios as in (*a*)

(*c*) A similar result was obtained when **1** (0 1 g) was treated with 2% methanolic hydrogen chloride (10 drops) in methanol (5 ml) at room temperature for 6 h

4,6-O-Isopropylidenesucrose hexa-acetate (**5**) — A solution of **2** (0 2 g) in pyridine (10 ml) was treated with acetic anhydride (1 ml) at room temperature for 20 h The solution was concentrated to give **5** (0 2 g, 87%) as a syrup The ^{1}H-n m r and mass spectra of **5** were indistinguishable from those of a standard sample[1]

1′2-Di-O-mesylsucrose hexa-acetate (**6**) — A solution of **2** (0 4 g) in pyridine (10 ml) was treated with mesyl chloride (2 ml) at 0°, and then stored at room temperature for 24 h T l c (ether–light petroleum, 6 1) showed a fast-moving product The solution was poured into ice–water and extracted with dichloromethane, and the extract was washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and concentrated The syrupy residue was then treated with 60% aqueous acetic acid (50 ml) at 100° for 15 min The solution was concentrated to dryness, the residue was treated with acetic anhydride (3 ml) and pyridine (20 ml) at room temperature for 24 h, and the solution was then concentrated to give **6** (0 3 g, 55%) The ^{1}H-n m r and mass spectra of **6** were identical with those of an authentic sample[4]

1′,2-O-Isopropylidenesucrose hexa-acetate (**7**) — A solution of **3** (1 6 g) in pyridine (20 ml) was treated with acetic anhydride (2 ml) at room temperature for 24 h The solution was then concentrated to give **7** (1 7 g, 92 1%) as a syrup, $[\alpha]_D$ +18° (*c* 0 88, chloroform) N m r data ($CDCl_3$) τ 3 83 (d, 1 H, $J_{1\,2}$ 3 5 Hz, H-1) 6 16 (q, 1 H, $J_{2\,3}$ 10 0 Hz, H-2), 4 67 (t, 1 H, $J_{3\,4}$ 10 0 Hz, H-3), 5 20 (t, 1 H, $J_{4\,5}$ 10 0 Hz, H-4), 4 84 (d, 1 H, $J_{3',4}$ 6 5 Hz, H-3′), 4 50–4 69 (m, 1 H, H-4′), 7 78–8 04 (18 H, 6 Ac), 8 55, and 8 80 (s, 6 H, 2 Me)

Anal Calc for $C_{27}H_{38}O_{17}$ C, 51 1, H, 6 0 Found C, 51 8, H, 6 2

3,4,6,3′,4′,6′-Hexa-O-acetylsucrose[4] (**8**) — A solution of **7** (1 2 g) in 60% aqueous acetic acid (60 ml) was kept at 90° for 15 min. T l c (ether–light petroleum, 6 1) revealed a slow-moving product The solution was concentrated to a syrup which, on crystallisation from ether, afforded **8** (0.7 g, 61 5%), m p. 123–125°; lit.[4] m p 118–119°. The ^{1}H-n m r. and mass spectra of **8** were indistinguishable from those of a standard sample[4]

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