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Note

Synthesis and reactions of sucrose-5- and 5'-enes*

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The potential value of unsaturated sugars as synthetic and biological intermediates is well-recognised[2,3] In continuation of our study on exocyclic vinyl ethers of carbohydrates[3–5], we now report the synthesis and reactions of β-D-fructofuranosyl 6-deoxy-α-D-*xylo*-hex-5-enopyranoside and α-D-glucopyranosyl 6-deoxy-β-D-*threo*-hex-5-enofuranoside

Selective tosylation of 1',2,3,3',4',6'-hexa-*O*-acetylsucrose[6] with 2 molar equivalents of toluene-*p*-sulphonyl chloride in pyridine gave the 6-sulphonate **1** in 77% yield Conventional acetylation of **1** with acetic anhydride and pyridine gave the corresponding hepta-acetate **2** The structure of **2** was supported by its ^{1}H-n m.r. spectrum, and its mass spectrum contained major peaks at *m/e* 443 and 331 due to hexopyranosyl and ketofuranosyl cations, respectively Nucleophilic displacement of the sulphonyloxy group in **2** by sodium iodide in butanone yielded the 6-iodide **3**, and treatment of **3** with anhydrous silver fluoride and pyridine for 16 h at room temperature afforded the 5-ene **4** in 60% yield. In the ^{1}H-n m r. spectrum of **4**, the resonances due to vinyl protons (H-6a, H-6b) appeared as triplets centered at τ 5.13 and 5 41, with splittings of 1 25–1 5 Hz presumably due to long-range allylic couplings between H-4 and protons at C-6 The structure of **4** was consistent with its mass-spectral data

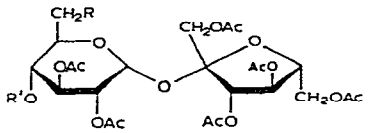
Hydrogenation of the 5-ene **4** over palladium-on-charcoal gave β-D-fructofuranosyl 6-deoxy-β-L-idopyranoside hepta-acetate (**5**) in 45% yield A similar hydrogenation of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-*xylo*-hex-5-enopyranoside has been reported to proceed stereospecifically to give methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-L-idopyranoside[7] When hydrogenation of the de-esterified derivative of **4** was performed over palladium-on-charcoal, it gave, after acetylation and chromatography, the L-*ido* isomer **5** and the D-*gluco* isomer **6** in yields of 45% and 10%, respectively. These results are consistent with our earlier observation that the proportion of each isomer is dependent upon the substituents on the vinyl ether[3].

The structure of **5** was supported by its ^{1}H-n m r spectrum, the derived first-order coupling constants ($J_{1,2}$ 2 0, $J_{2,3} = J_{3,4} = 3$ 5, and $J_{4,5}$ 2 5 Hz) revealed the

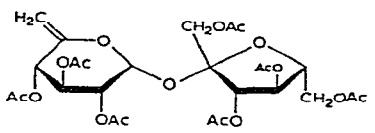
*Sucrochemistry Part XXII For Part XXI, see Ref 1

L-*ido* configuration and $^1C_4$ conformation for the hexopyranose moiety The mass spectrum of **5** contained a strong peak at *m/e* 331 due to the ketofuranosyl cation, and a weaker at *m/e* 273 due to the hexopyranosyl cation The structure of **6** was also supported by its ^{1}H-n m r spectrum; the coupling constants for the hexopyranose moiety were consistent with the *gluco* configuration

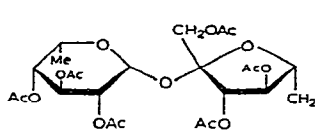
Compound **6** was also synthesised by reductive dehalogenation of the 6-iodide **3** with Raney nickel and hydrazine hydrate in the presence of barium carbonate.



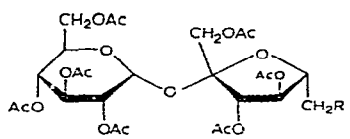
1 R = OTs R′ = H
2 R = OTs R = Ac
3 R = I R = Ac
6 R = H R = Ac



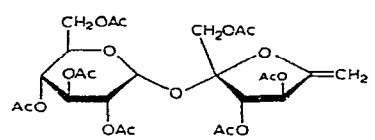
4



5



7 R = OTs
8 R = I
10 R = H



9

Synthesis of α-D-glucopyranosyl 6-deoxy-β-D-*threo*-hex-5-enofuranoside hepta-acetate (**9**) was achieved by the following sequence of reactions 1′,2,3,3′,4,4′,6-hepta-*O*-acetylsucrose[8] → 6′-*O*-tosylsucrose hepta-acetate (**7**) → 6′-deoxy-6′-iodosucrose hepta-acetate (**8**) → **9** The structures of compounds **7–9** were supported by their ^{1}H-n m r and mass spectra The ^{1}H-n m r spectrum of the 5′-ene **9** showed the well-known[3] allylic coupling (*J* 1 5–1 75 Hz) between the hydrogens of C-4′ and C-6′ Hydrogenation of **9** over palladium-on-charcoal afforded exclusively 6′-deoxysucrose hepta-acetate (**10**, 99%), the structure of which was confirmed by ^{1}H-n m r and mass spectrometry, and by an alternative synthesis Reductive dehalogenation of the 6′-iodide **8**, using Raney nickel and hydrazine hydrate, gave **10** in 71% yield.

EXPERIMENTAL

For details of general procedure, see Part VI[9].

1′,2,3,3′,4′,6′-Hexa-O-*acetyl-6*-O-*tosylsucrose* (**1**) — Solutions of 1′,2,3,3′,4′,6′-hexa-*O*-acetylsucrose (8.5 g) in pyridine (200 ml) and toluene-*p*-sulphonyl chloride (6 g) in pyridine (25 ml) were mixed and stirred initially at 0° for 1 h and then at room

temperature for 30 h The reaction mixture was poured into ice–water, the resulting precipitate was taken up in dichloromethane, and the organic layer was washed with water and aqueous sodium hydrogen carbonate, and dried (Na_2SO_4) The solution was concentrated to give **1** (8 2 g, 77%), m p 53–55° (from ether), $[\alpha]_D$ +49 2° (*c* 1 02, chloroform) N m r data τ 4 43 (d, 1 H, $J_{1,2}$ 3 5 Hz, H-1), 5 29 (q, 1 H, $J_{2,3}$ 10 0 Hz, H-2), 4 65 (q, 1 H, $J_{3,4}$ 9 5 Hz, H-3), 4 59 (d, 1 H, $J_{3',4}$ 5 0 Hz, H-3'), 4 7 (t, 1 H, $J_{4,5}$ 5 0 Hz, H-4'), 7 52 (s 3 H, Me); 7 84–7 89 (18 H, 6 Ac), 2 15–2 69 (4 H, Ar*H*) Mass-spectral data [(a) indicates ions due to hexopyranosyl and (*b*) due to ketofuranosyl cations] *m/e* 401a, 341a, 331b, 299a, 289b, 281a, 271b, 229b, 211b, 169b, 127b, and 109b

Anal Calc for $C_{31}H_{40}O_{19}S$ C, 49 73, H, 5 39, S, 4 28 Found C, 49 56, H, 5 21, S, 4 22

6-O-Tosylsucrose hepta-acetate (**2**) — A solution of **1** (4 g) in pyridine (50 ml) was treated with acetic anhydride (5 ml) at room temperature for 16 h The reaction mixture was poured into ice–water, the precipitate was taken up in dichloromethane, and the solution was washed with water, dried (Na_2SO_4), and concentrated to afford **3** (4 g, 95%) as a syrup, $[\alpha]_D$ +60 5° (*c* 1 01, chloroform), lit [10] +23° (*c* 0 4, chloroform) N m r data τ 4 35 (d, 1 H, $J_{1,2}$ 3 75 Hz, H-1), 5 23 (q, 1 H, $J_{2,3}$ 10 0 Hz, H-2), 4 56 (t, 1 H, $J_{3,4}$ 10 0 Hz, H-3), 4 98 (t, 1 H, $J_{4,5}$ 10 0 Hz, H-4), 4 62 (d, 1 H, $J_{3',4'}$ 6 0 Hz, H-3'), 4 58 (t, 1 H, $J_{4',5'}$ 6 0 Hz, H-4'), 7 52 (s, 3 H, Me), 7.8, 7 84, 7 87, 7 86, 7 9, 7 96, 7 98 (7 s, 21 H, 7 Ac),2 15–2 68 (4 H, Ar*H*) Mass-spectral data [(a) and (b) represent hexopyranosyl and ketofuranosyl cations, respectively] *m/e* 443a, 383a, 331b, 323a, 281a, 211b, 169b, 127b, 109b, and 101

Anal. Calc for $C_{33}H_{42}O_{20}S$ C, 50 1, H, 5 35, S, 4 05 Found C, 50 6, H, 5 47, S, 4 0.

6-Deoxy-6-iodosucrose hepta-acetate (**3**) — A solution of **2** (4 g) in butanone (50 ml) was boiled in the presence of sodium iodide (4 g) for 20 h T l c (ether–light petroleum, 4 1) showed a fast-moving, major product The solution was diluted with ether and the solid residue was filtered off The solution was then concentrated to a syrup that was eluted from a column of silica gel, using ether–light petroleum (1 1), to give **3** (3 2 g, 85%), m p 79–81°, $[\alpha]_D$ +61 8° (*c* 1 06, chloroform), lit [10] +58 8° (*c* 0 37, chloroform) N m r data τ 4 28 (d, 1 H, $J_{1,2}$ 3 5 Hz, H-1), 5 17 (q, 1 H, $J_{2,3}$ 10 0 Hz, H-2), 4 54 (q, 1 H, $J_{3,4}$ 9 5 Hz, H-3), 5 03 (t, 1 H, $J_{4,5}$ 9 5 Hz, H-4), 4 56 (d, 1 H, $J_{3',4}$ 5 0 Hz, H-3'), 7 83, 7 85, 7.89, 7 9, 7 91, 7 95, 7 99 (7 s, 21 H, 7 Ac) Mass-spectral data [(a) and (b) indicate hexopyranosyl and ketofuranosyl cations, respectively] *m/e* 399a, 339a, 331b, 297a, 279a, 271b, 237a, 211b, 169b, and 109

Anal Calc for $C_{26}H_{35}IO_{17}$ C, 41 8; H, 4 69, I, 17 0. Found. C, 42 8, H, 4 83, I, 16 8

*6-Deoxy-α-*D*-xylo-hex-5-enopyranosyl β-*D*-fructofuranoside hepta-acetate* (**4**) — A solution of **3** (1 g) in pyridine (20 ml) was shaken with anhydrous silver fluoride (1 g) at room temperature for 16 h The reaction mixture was then diluted with ether, the insoluble silver salt filtered off, and the filtrate concentrated. The syrupy residue

was eluted from a small column of silica gel, using ether–light petroleum (2·1), to afford **4** (0 5 g, 60%) as a syrup, $[\alpha]_D$ +31 6° (*c* 1.1, chloroform) N m r. data· τ 4 29 (d, 1 H, $J_{1,2}$ 3 25 Hz, H-1); 5 01 (q, 1 H, $J_{2,3}$ 10 25 Hz, H-2); 4 59 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.45–4 6 (H-4); 5 13, 5 41 (H-6a,6b); 7.78–7.98 (21 H, 7 Ac). Mass-spectral data [(a) and (b) represent hexopyranosyl and ketofuranosyl cations, respectively] *m/e* 331 b, 271 a, 211, 169, 127, 109, and 101.

Anal Calc for $C_{26}H_{34}O_{17}$ C, 50 5; H, 5 5. Found C, 50 7; H, 5 3.

Hydrogenation of the 5-ene **4** — A solution of **4** (1 1 g) in ethyl acetate and methanol (1 1, 40 ml) was hydrogenated in the presence of palladium-on-charcoal (1 g) at 60 p s i for 6 h The catalyst was filtered off and the filtrate concentrated. The syrupy residue was then eluted from a column of silica gel, using ether–light petroleum (1 1), to give 6-deoxy-β-L-idopyranosyl β-D-fructofuranoside hepta-acetate **5** (0.5 g, 45%), m p 176–179° (from ether), $[\alpha]_D$ −1.44° (*c* 1.1, chloroform). N m r. data τ 4 79 (d, 1 H, $J_{1,2}$ 2 0 Hz, H-1); 5.13 (q, 1 H, $J_{2,3}$ 3 5 Hz, H-2); 4 91 (t, 1 H, $J_{3,4}$ 3 5 Hz, H-3); 5 31 (q, 1 H, $J_{4,5}$ 2 5 Hz, H-4); 4 45–4 52 (H-3′,4′); 8 82–8 94 (21 H, 7 Ac), 8 7 (d, 3 H, Me) Mass-spectral data [(a) and (b) indicate ions due to hexopyranosyl and ketofuranosyl cations, respectively]. *m/e* 331 b, 273 a, 271 a, 213 a, 211 b, 171 a, 169 b, 153 a, 111 a, 109 b, and 101.

Anal Calc. for $C_{26}H_{36}O_{17}$: C, 50 3; H, 5 8. Found C, 50 6, H, 6 0.

Hydrogenation of the de-esterified derivative of **4** — A solution of the 5-ene **4** (1.5 g) in dry methanol was treated with a catalytic amount of sodium methoxide in methanol at room temperature for 16 h T.l c (chloroform–methanol, 3 1) then showed a single spot The solution was concentrated, after treatment with Amberlyst 15 (H^+) resin A solution of the syrupy residue in ethyl acetate and methanol (1 1, 100 ml) was then hydrogenated in the presence of palladium-on-charcoal at 60 p s i. for 6 h. The reaction was worked-up as described previously, and the syrupy product was conventionally acetylated with acetic anhydride and pyridine Elution of the product from a column of silica gel, with ether–light petroleum (1 1), gave, in addition to the L-*ido* isomer **5** (0 83 g, 46%), 6-deoxysucrose hepta-acetate **6** (0 18 g, 10%), $[\alpha]_D$ +61 6° (*c* 1 06, chloroform), lit.[10] $[\alpha]_D$ +90 0° (*c* 0 88, chloroform) N m r. data. τ 4.4 (d, 1 H, $J_{1,2}$ 3 75 Hz, H-1); 5 18 (q, 1 H, $J_{2,3}$ 10 5 Hz, H-2); 4.61 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5 2 (t, 1 H, $J_{4,5}$ 9 5 Hz, H-4); 4 57 (d, 1 H, $J_{3',4'}$ 6 0 Hz, H-3′), 4 64 (t, 1 H, $J_{4',5'}$ 6 0 Hz, H-4′), 8 78 (d, 3 H, Me); 7.84–8.0 (21 H, 7 Ac) Mass-spectral data [(a) and (b) represent ions due to hexopyranosyl and ketofuranosyl cations, respectively] *m/e* 331 b, 289 b, 273 a, 271 b, 213 a, 211 b, 171 a, 169 b, 153 a, 127 b, 111 a, 109 b, and 101.

Anal. Calc for $C_{26}H_{36}O_{17}$ C, 50 3; H, 5.8. Found C, 50.7; H, 6.1.

6-Deoxysucrose hepta-acetate (**6**). — A solution of **3** (1 g) in ethyl acetate and methanol (1 1, 100 ml) was boiled in the presence of Raney nickel catalyst (500 mg), hydrazine hydrate (6.5 ml), and barium carbonate (6 g) for 1 h. The reaction mixture was filtered through "Hyflo" and concentrated, and the residue was conventionally acetylated with acetic anhydride and pyridine. Chromatography of the product on a column of silica gel, with ether–light petroleum (1·1), gave **6** (0.63 g, 75%), $[\alpha]_D$ +62°

(*c* 1.04, chloroform) The ^{1}H-n m r. and mass-spectral data were identical with those of the sample **6** prepared previously.

6'-O-Tosylsucrose hepta-acetate (**7**). — A solution of 1',2,3,3',4,4',6-hepta-*O*-acetylsucrose (2 3 g) in pyridine (50 ml) was treated with toluene-*p*-sulphonyl chloride (6 g) at 0°. After storage for 16 h at room temperature, the reaction mixture was worked-up as described previously to give **7** (2 25 g, 79%) as an amorphous powder, $[\alpha]_D$ +47.8° (*c* 0 95, chloroform). N m.r. data (C_6D_6) τ 4 48 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1); 5 06 (q, 1 H, $J_{2,3}$ 10 5 Hz, H-2); 4 28 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3); 4 8 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4); 4 33 (d, 1 H, $J_{3',4'}$ 5 75 Hz, H-3'), 4 61 (t, 1 H, $J_{4',5'}$ 5.75 Hz, H-4'); 7 54 (s, 3 H, Me); 8 04–8 40 (21 H, 7 Ac); 2 13–3.17 (4 H, Ar*H*). Mass-spectral data [(a) and (b) ions indicate hexopyranosyl and ketofuranosyl cations, respectively]. *m/e* 443b, 331a, 323b, 271a, 211a, 169a, 127a, and 109a

Anal. Calc for $C_{33}H_{42}O_{20}S$· C, 50 1, H, 5 35; S, 4 05. Found C, 51 0; H, 5 51; S, 4.29.

6'-Deoxy-6'-iodosucrose hepta-acetate (**8**). — Treatment of **7** (2.25 g) with sodium iodide (2 25 g) in boiling butanone (40 ml) for 20 h gave, after work-up as described for **3**, **8** (1.8 g), m p. 78–80° (from ether–light petroleum), $[\alpha]_D$ +38 4° (*c* 1.02, chloroform) N m r. data τ 4 38 (d, 1 H, $J_{1,2}$ 3 7 Hz, H-1), 5 15 (q, 1 H, $J_{2,3}$ 10.0 Hz, H-2); 4 56 (q, $J_{3,4}$ 9 5 Hz, H-3), 4 96 (t, 1 H, $J_{4,5}$ 9 5 Hz, H-4), 4.58 (d, 1 H, $J_{3',4'}$ 5.0 Hz, H-3'); 4 7 (t, 1 H, $J_{4',5'}$ 5 0 Hz, H-4'); 7 84–7.99 (21 H, 7 Ac) Mass-spectral data [(a) and (b) indicate ions due to hexopyranosyl and ketofuranosyl cations, respectively] *m/e* 399b, 339b, 331a, 297b, 279b, 271a, 255b, 237b, 229a, 213b, 211a, 195b, 187a, 169a, 145a, 127a, 109a, and 101.

Anal. Calc for $C_{26}H_{35}IO_{17}$ C, 41 8, H, 4 7; I, 17 0. Found. C, 41 8; H, 4 9; I, 17.3.

α-D-Glucopyranosyl 6-deoxy-β-D-threo-hex-5-enofuranoside hepta-acetate (**9**). — A mixture of **8** (1 g), pyridine (15 ml), and anhydrous silver fluoride (1 g) was shaken at room temperature for 16 h. The reaction mixture was worked-up as described for **4** to give **9** (600 mg, 72%), m.p. 158–160° (from ether), $[\alpha]_D$ +59 9° (*c* 1.05, chloroform). N.m.r. data. τ 4 37 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1); 5 15 (q, 1 H, $J_{2,3}$ 10 0 Hz, H-2), 4 54 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.92 (t, 1 H, $J_{4,5}$ 9 5 Hz, H-4); 4 63 (d, 1 H, $J_{3',4'}$ 5 0 Hz, H-3'); 4 2 (d, 1 H, $J_{4',5'}$ 5 0 Hz, H-4'); 5 4, 5.7 (2 H, H-6a,6b); 7.84–8.0 (21 H, 7 Ac). Mass-spectral data [(a) and (b) represent ions due to hexopyranosyl and ketofuranosyl cations, respectively]· *m/e* 331a, 271b, 229, 211, 187, 169, 145, 127, 109, and 101.

Anal. Calc for $C_{26}H_{34}O_{17}$· C, 50 5; H, 5.5. Found· C, 50 42; H, 5.56.

Hydrogenation of the 5'-ene **9**.— A solution of **9** (200 mg) in ethyl acetate–methanol (1.1, 10 ml) was hydrogenated in the presence of palladium-on-charcoal at 60 p.s.i for 6 h The catalyst was filtered off and the filtrate concentrated to give **10** (200 mg, 99%), m p. 135–137° (from ether), $[\alpha]_D$ +59.7° (*c* 1, chloroform). N.m r. data. τ 4 38 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1); 5.13 (q, $J_{2,3}$ 10.5 Hz, H-2); 4 55 (q, 1 H, $J_{3,4}$ 9.5 Hz, H-3); 4.93 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4); 4 59 (d, 1 H, $J_{3',4'}$ 6 5 Hz, H-3'); 4.81 (t, 1 H, $J_{4',5'}$ 6.5 Hz, H-4'); 8 57 (d, 3 H, Me); 7.82–7.98 (21 H, 7 Ac). Mass-

spectral data [(a) and (b) indicate ions due to hexopyranosyl and ketofuranosyl cations respectively] *m/e* 331a, 289a, 273b, 271a, 229a, 213b, 211a, 187a, 171b, 169a, 153b, 145a, 127a, 111b, 109a, and 101.

Anal Calc for $C_{26}H_{36}O_{17}$. C, 50 3; H, 5.8. Found C, 49 9; H, 5 8

6'-Deoxysucrose hepta-acetate (**10**) — A solution of the 6-iodide **8** (0 85 g) in ethyl acetate and methanol (1 1, 100 ml) was boiled in the presence of Raney nickel catalyst (1 g), hydrazine hydrate (6 5 ml), and barium carbonate (6 g) for 1 h. The mixture was worked-up as described previously to afford a syrupy residue that was conventionally acetylated with acetic anhydride and pyridine Elution of the product from a column of silica gel with ether–light petroleum (1.1) gave **10** (0 5 g, 71%), m p and mixture m p 135–137°, $[\alpha]_D$ +59 9° (*c* 1 04, chloroform). The ^{1}H-n m r. and mass-spectral data were identical with those of the sample **10** prepared previously.

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