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SYNTHESIS OF 3-, 4-, AND 6-MONODEOXYSUCROSES*†

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ABSTRACT

A divergent synthesis of 6-deoxy (**5**), 4-deoxy (**9**), and 3-deoxy (**15**) derivatives of sucrose, after acetalation of sucrose with 2,2-dimethoxypropane, is detailed. Thus, **5** was prepared by hydrogenolysis of 6-*S*-(2-pyridyl)-6-thiosucrose, whereas **9** and **15** were obtained by radical reduction of the corresponding thiocarbonyl derivatives.

INTRODUCTION

During its transport in plants, sucrose is specifically and reversibly bonded to a carrier protein[2], through hydrogen bonds and hydrophobic interactions.

In order to determine the relative importance of interaction for each hydroxyl group of the sugar moiety, the synthesis of monodeoxysucroses as competitive substrate-inhibitors was of interest. Accessibility to protected sucroses having only one available hydroxyl group is required for the construction of sucrose analogues with altered overall hydrophilic–hydrophobic and hydrogen-bonding, and, hence binding characteristics[3].

Some sucrose derivatives modified at the fructofuranosyl moiety have already been studied[4], and in order to extend this study to the pyranosyl part, we now report the synthesis of 3-, 4-, and 6-monodeoxysucroses.

Although the synthesis of several deoxysucroses[5,6] have been already published, this report describes a unique synthetic pathway in which the three deoxysucroses are derived from the same intermediate step of sucrose acetalation.

RESULTS AND DISCUSSION

The deoxysucroses were prepared from one of the two major products

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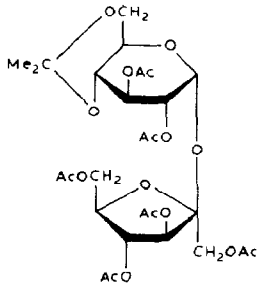
obtained by acetalation of sucrose with 2,2-dimethoxypropane[7,9], namely, 2,3,1′,3′,4′,6′-hexa-*O*-acetyl-4,6-*O*-isopropylidenesucrose* (**1**) and 3,3′,4′,6′-tetra-*O*-acetyl-1′,2:4,6-di-*O*-isopropylidenesucrose (**2**). Both compounds were suitable for our purpose, but a more-selective[10] synthesis of the mono or the diisopropylidenesucrose may be used if only one of these compounds is required.

6-Deoxysucrose (**5**) and 4-deoxysucrose (**9**) were prepared from 2,3,1′,3′,4′,6′-hexa-*O*-acetylsucrose (**3**). Selective *S*-pyridylation[11] of **3** with 2 equivalents of 2,2′-dipyridyl disulfide and 3 equivalents of tributylphosphine gave 2,3,1′,3′,4′,6′-hexa-*O*-acetyl-6-*S*-(pyridyl)-6-thiosucrose (**4**) in 41% yield, together with a small proportion of a disubstituted compound identified as 1,3,4,6-tetra-*O*-acetyl-β-D-fructofuranosyl 2,3-di-*O*-acetyl-4,6-di-*S*-(2-pyridyl)-4,6-dithio-α-D-galactopyranoside (**16**). The latter became the main product (79% from **3**) when



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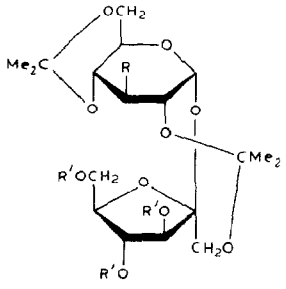
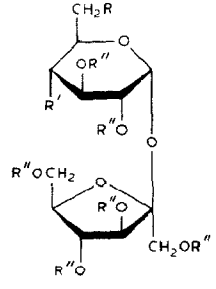
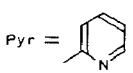
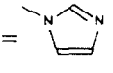


2 R = OAc, R′ = Ac
10 R = OAc, R′ = H
11 R = OAc, R′ = TBDMS
12 R = OH, R′ = TBDMS
13 R = OCSIm, R′ = TBDMS
14 R = H, R′ = TBDMS

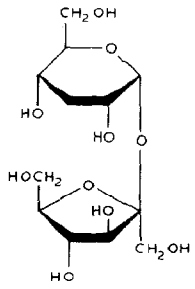


3 R = R′ = OH, R″ = Ac
4 R = SPyr, R′ = OH, R″ = Ac
5 R = R″ = H, R′ = OH
6 R = OAc, R′ = OH, R″ = Ac
7 R = OAc, R′ = CSIm, R″ = Ac
8 R = OAc, R′ = H, R″ = Ac
9 R = OH, R′ = R″ = H

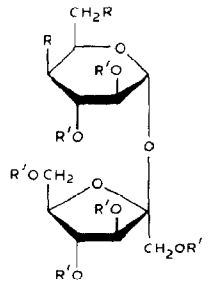




TBDMS = Me_3CSiMe_2—



15



16 R = SPyr, R′ = Ac
17 R = R′ = H

*Primed substituents refer to the fructose residue.

more-vigorous conditions are used. As anticipated from mechanistic considerations[11], the nucleophilic substitution at C-4 proceeds with inversion of configuration. The *galacto* configuration of **16** was assigned from the first-order $J_{3,4}$ coupling constant (4.15 Hz) characteristic of the equatorial arrangement of H-4 in the $^4C_1$(D) conformation of compound[12] **16**. This disubstituted product was reduced and deacetylated conventionally to give 4,6-dideoxysucrose (**17**). The ^{13}C-n.m.r. spectra of these compounds (Table I) are also in accord with the proposed structures.

Reduction of the *S*-pyridyl group of **4** was accomplished with Raney nickel W4 to give, after deprotection, 6-deoxysucrose (**5**).

TABLE I

^{13}C-N.M.R. CHEMICAL-SHIFT DATA FOR **4–9** AND **15–17** (δ IN P.P.M.)

	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*
4[a]	91.1	71.8[d]	71.1[d]	72.3[d]	69.8[d]	32.5	63.0[e]	104.8	76.1[f]	76.5[f]	80.1	63.7[e]
5[b]	94.8	76.8[d]	75.7[d]	74.1[d]	71.2[d]	19.5	63.8[e]	106.5	79.1	77.9	84.1	65.2[e]
6[c]	90.8	71.5[d]	71.1[d]	72.4[d]	69.2[d]	63.0[e]	63.5[e]	104.5	75.8[f]	76.2[f]	79.7	64.3[e]
7[c]	90.6	70.5[d]	69.5[d]	77.5	68.3[d]	62.4[e]	62.4[e]	105.1	75.8[f]	76.3[f]	*80.2*	*64.0*[e]
8[c]	91.3	71.7	67.3[d]	32.7	66.7[d]	63.2[e]	64.5[e]	103.9	75.4[f]	75.9[f]	79.1	65.6[e]
9[b]	95.5	75.7[d]	72.1[d]	36.9	69.5[d]	64.2[e]	66.2[e]	106.3	79.3[f]	76.8[f]	84.0	65.0[e]
15[b]	92.0	67.3[d]	35.1	65.0[d]	74.2	61.3[e]	62.5[e]	104.7	77.5[f]	75.1[f]	82.5	63.5[e]
16[a]	91.8	70.6[d]	69.7[d]	48.9	69.3[d]	31.6	63.8[e]	104.5	76.3[f]	76.7[f]	79.9	64.6[e]
17[b]	95.5	75.7[d]	69.6[d]	42.7	68.4[d]	22.7	64.9[e]	106.2	79.3[f]	76.7[f]	84.1	64.0[e]

[a]In $CDCl_3$. [b]In D_2O. [c]In C_6D_6. [d,e,f]Assignments marked with identical letters may be interchanged.

A sucrose derivative having the 4-hydroxyl group free is generally prepared[7] by tritylation of the hexaacetate **3**. The tritylation and subsequent detritylation steps may be avoided by direct, selective 6-*O*-acetylation of **3** with 1.5 equivalents of acetyl chloride at −78°, which gave 1',2,3,3',4',6,6'-hepta-*O*-acetylsucrose (**6**) in 60% yield. The regioselectivity of the acylation of compound **3** was supported by the ^{1}H-n.m.r. spectrum of **6**; the H-4 resonance appeared at relatively high field (δ 3.5) in comparison with the H-4 signal in sucrose octaacetate (δ 5.3), indicating that O-4 was not acetylated. Compound **6** was thiocarbonylated and then reduced at C-4 by tributyltin hydride in toluene[13] to give, after deacetylation, 4-deoxysucrose (**9**).

3-Deoxysucrose (**15**) was prepared from 3,3',4',6'-tetra-*O*-acetyl-1',2:4,6-di-*O*-isopropylidenesucrose (**2**). Binder and Robyt[5] reported the synthesis of 3-*O*-benzoyl-1',2:4,6-di-*O*-isopropylidenesucrose in moderate yield from 3,3',4',6'-tetra-*O*-benzoyl-1',2:4,6-di-*O*-isopropylidenesucrose. 3-*O*-Acetyl-1',2:4,6-di-*O*-isopropylidenesucrose (**10**) was obtained in 80% yield by regioselective deacetylation with sodium methoxide. Silylation of **10** to give **11** by standard methods (*tert*-butylchlorodimethylsilane and imidazole[14]) was preferred to benzylation. The tri-

ether **11** was then deacetylated and thiocarbonylated at C-3, to give after classical reduction with tributyltin hydride, 3′,4′,6′-tri-*O*-*tert*-butyldimethylsilyl-3-deoxy-1′,2:4,6-di-*O*-isopropylidenesucrose (**14**). Two-step removal of the protecting groups from **14** (desilylation with tetrabutylammonium fluoride and deacetalation with aqueous acetic acid) gave 3-deoxysucrose (**15**).

EXPERIMENTAL

General methods. — Optical rotations were measured with a Perkin–Elmer 241 polarimeter at ambient temperatures (22 ±2°). T.l.c. was performed on precoated plates of Silica Gel 60-F 254 (E. Merck, Darmstadt) with 10% H_2SO_4 in EtOH. Column chromatography was performed on Matrex Silica 35-70 MY from Amicon. ^{1}H-N.m.r. spectra were recorded on Bruker AM 300 or Bruker WP 80 instruments with Me_4Si as the internal standard for $CDCl_3$ and C_6D_6 solutions. The reference standard for D_2O solutions was sodium 4,4-dimethyl-4-silapentanoate-2,2,3,3-d_4. ^{13}C-N.m.r. spectra were recorded at 75 MHz (Bruker AM-300 spectrometer) using Me_4Si as the internal standard for C_6D_6 and $CDCl_3$ solutions and sodium 4,4-dimethyl-4-silapentanoate-2,2,3,3-d_4 for D_2O solutions. Evaporations were performed under diminished pressure.

*2,3,1′,3′,4′,6′-Hexa-*O*-acetyl-1′,2-*O*-isopropylidenesucrose* (**1**) *and 3,3′,4′,6′-tetra-*O*-acetyl-1′,2:4,6-di-*O*-isopropylidenesucrose* (**2**). — A solution of sucrose (20 g) in *N,N*-dimethylformamide (250 mL) was stirred with 2,2-dimethoxypropane (100 mL) and *p*-toluenesulfonic acid (0.6 g) for 1 h at room temperature, and then made neutral by stirring with $NaHCO_3$ (5 g) for 30 min. The mixture was filtered, and the filtrate evaporated at 60–70°. The resulting syrup was treated with Ac_2O (80 mL) and C_5H_5N (250 mL) for 16 h at room temperature. The mixture was then evaporated by codistillation with toluene, and the residue eluted from a column of silica gel with 3:1 ether–light petroleum to afford the following products:

2,3,1′,3′,4′,6′-Hexa-*O*-acetyl-1′,2-*O*-isopropylidenesucrose (**1**; 13 g, 35%), $[\alpha]_D$ +42° (*c* 1.2, $CHCl_3$); lit.[7] $[\alpha]_D$ +46° (*c* 0.2, $CHCl_3$); the ^{1}H-n.m.r. data were similar to those previously reported[7].

3,3′,4′,6′-Tetra-*O*-acetyl-1′,2:4,6-di-*O*-isopropylidenesucrose (**2**; 13.1 g, 38%); m.p. 135–136°, $[\alpha]_D$ +16° (*c* 1.0, $CHCl_3$); lit.[9] m.p. 136–137°, $[\alpha]_D$ +12.8° (*c* 1.0, $CHCl_3$); the ^{1}H-n.m.r. data were similar to those previously reported[9].

*2,3,1′,3′,4′,6′-Hexa-*O*-acetylsucrose* (**3**). — A solution of **1** (6.1 g) in 60% aq. HOAc (150 mL) was kept for 10 min at 80°. The solution was evaporated by codistillation with toluene to give **3** (5.5 g, 96%); the ^{1}H-n.m.r. data were similar to those previously reported[7].

*2,3,1′,3′,4′,6′-Hexa-*O*-acetyl-6-*S*-(2-pyridyl)-6-thiosucrose* (**4**). — A solution of **3** (5 g) in pyridine (100 mL) was stirred with 2,2′-dipyridyl disulfide (3.7 g) and Bu_3P[10] (4 mL) for 30 min at room temperature. Water (5 mL) was then added to stop the reaction. The solution was evaporated by codistillation with toluene and the resulting syrup was eluted from a column of silica gel with ether to give **4** (2.4

g, 41%); $[\alpha]_D$ −22.1° (*c* 0.8, $CHCl_3$); ^{1}H-n.m.r. data (C_6D_6): δ 7.8 (d, 1 H, H-α), 6.7–6.1 (3 H-β,β′,γ), 6.1–5.5 (4 H, H-1,3,3′,4′), 5.1 (dd, 1 H, H-2), 4.9–3.3 (8 H, H-5,6a,6b,1′a,1′b,5′,6′a,6′b), and 2–1.5 (6 s, 18 H, 6 Ac).

Anal. Calc. for $C_{29}H_{37}NO_{16}S$: C, 50.65; H, 5.42. Found: C, 50.42; H, 5.38.

6-Deoxysucrose (**5**). — A solution of **4** (1.8 g) in EtOH (25 mL) was boiled for 90 min under reflux with freshly prepared Raney nickel W4 (38 g). The mixture was filtered and the filtrate evaporated. The resulting syrup was then treated with M methanolic NaOMe (2 mL) in boiling MeOH (15 mL) for 10 min. The solution was made neutral by stirring with Amberlite IR-120 (H^+) resin for 10 min. The resin was removed and the filtrate evaporated to a syrup that crystallized from 1:2 EtOH–ether (1:2) to give **5** (0.55 g, 64%), m.p. 170–175°, $[\alpha]_D$ +54.3° (*c* 0.95, water); lit.[4] m.p. 172–180° (from EtOH), $[\alpha]_D$ +54.8° (*c* 1.03, H_2O); ^{1}H-n.m.r. data (D_2O): δ 5.34 (d, 1 H, H-1), 4.23 (d, 1 H, H-3′), 4.06 (t, 1 H, H-4′), 3.94–3.67 (m, 7 H, H-3,5,1′a,1′b,5′,6′a,6′b), 3.56 (dd, 1 H, H-2), 3.16 (dd, 1 H, H-4), and 1.28 (d, 3 H, Me-6).

Anal. Calc. for $C_{12}H_{22}O_{10}$: C, 44.17; H, 6.79. Found: C, 44.03; H, 6.87.

2,3,6,1′,3′,4′,6′-Hepta-O-acetylsucrose (**6**). — A solution of AcCl (1 mL) and pyridine (3.5 mL) in dry CH_2Cl_2 (10 mL) was added to a solution of **3** (6 g) in dry CH_2Cl_2 (50 mL), during 30 min at −78°. The solution was kept for 4 h at −78°. Water (5 mL) was then added, the mixture was allowed to attain room temperature, and it was then evaporated. The residue was eluted from a column of silica gel with ether to give **6** (3.8 g, 59%), $[\alpha]_D$ +48.4° (*c* 0.6, $CHCl_3$); ^{1}H-n.m.r. data (C_6D_6): δ 5.8–5.3 (4 H, H-1,3,3′,4′), 4.9 (dd, 1 H, H-2), 4–4.7 (8 H, H-5,6a,6b,1′a,1′b,5′,6′a,6′b), 3.5 (dd, 1 H, H-4), and 1.4–2 (7 s, 21 H, 7 Ac).

Anal. Calc. for $C_{26}H_{36}O_{18}$: C, 49.05; H, 5.70. Found: C, 48.81; H, 5.62.

2,3,6,1′,3′,4′,6′-Hepta-O-acetyl-4-O-imidazolylthiocarbonylsucrose (**7**). — A solution of **6** (2.9 g) and thiocarbonyldiimidazole (2.1 g) in dry 1,2-dichloroethane (100 mL) was boiled under reflux for 12 h. The solution was evaporated and the residue was dissolved in CH_2Cl_2 (25 mL). The solution was washed with M HCl (25 mL), saturated $NaHCO_3$ (25 mL), and water (25 mL), dried (Na_2SO_4) and evaporated to give **7** (2.76 g, 81%), $[\alpha]_D$ +48.8° (*c* 0.8), $CHCl_3$; ^{1}H-n.m.r. data (C_6D_6): δ 6.3–5.3 (6 H, H-1,2,3,4,3′,4′), 5.2–4 (8 H, H-1′a,1′b,5,5′,6a,6′a,6b,6′b), and 2–1.4 (21 H, 7 Ac).

Anal. Calc. for $C_{30}H_{38}N_2O_{18}S$: C, 48.25; H, 5.13; N, 3.75; O, 38.57; S, 4.29. Found: C, 48.02; H, 5.14; N, 3.77; O, 39.06; S, 4.01.

2,3,6,1′,3′,4′,6′-Hepta-O-acetyl-4-deoxysucrose (**8**). — A solution of **7** (2.2 g) in dry PhMe (50 mL) was added under N_2, to a refluxing solution of Bu_3SnH (1.2 mL) in PhMe[6] (50 mL) during 1 h. The solution was boiled for 8 h under reflux and then evaporated. The residue was eluted from a column of silica gel with ether to give **8** (1.56 g, 83%), $[\alpha]_D$ +65.5° (*c* 0.84, $CHCl_3$); ^{1}H-N.m.r. data (C_6D_6): δ 6.0–5.3 (4 H), 5.0 (dd, 1 H, H-2), 4.7–3.8 (10 H), and 2.2–1.5 (7 s, 21 H, 7 Ac).

Anal. Calc. for $C_{26}H_{36}O_{17}$: C, 50.32; H, 5.84. Found: C, 49.61; H, 5.45.

4-Deoxysucrose (**9**). — To a solution of **8** (1.23 g) in dry MeOH (8 mL) was

added M methanolic NaOMe (1 mL). The solution was stirred for 20 min at room temperature. During the reaction, **9** (0.52 g, 81.2%) crystallized; m.p. 190–195° (from MeOH), $[\alpha]_D$ +64.4° (*c* 1, H_2O); lit.[6] m.p. 181–182° (from EtOH), $[\alpha]_D$ +54° (*c* 1, MeOH); ^{1}H-n.m.r. data (D_2O): δ 5.43 (d, 1 H, H-1), 4.2–3.5 (12 H), 2.0 (dd, 1 H, H-4*e*), and 1.48 (q, 1 H, H-4*a*).

Anal. Calc. for $C_{12}H_{22}O_{10}$: C, 44.17; H, 6.79. Found: C, 44.33; H, 6.71.

3-O-Acetyl-1',2:4,6-di-O-isopropylidenesucrose (**10**). — This compound was prepared by the following modifications of the procedure previously reported[8]. A solution of **2** (3.6 g) in dry MeOH (50 mL) was stirred with M methanolic NaOMe (5 mL) for 90 min at room temperature, and then neutralized by stirring with Amberlite IR-120 (H^+) resin for 15 min. The resin was filtered off and the filtrate evaporated. The residue was eluted from a column of silica gel with EtOAc, to give **10** (2.25 g, 80%), $[\alpha]_D$ +29.9° (*c* 1.1, $CHCl_3$); lit.[8] $[\alpha]_D$ +28° (*c* 1.2, $CHCl_3$); the ^{1}H-n.m.r. data were similar to those previously reported[8].

*3-O-Acetyl-3',4',6'-tri-O-*tert*-butyldimethylsilyl-1'2:4,6-di-O-isopropylidenesucrose* (**11**). — A solution of **10** (5.8 g) in *N,N*-dimethylformamide (100 mL) was stirred with *tert*-butylchlorodimethylsilane (6.5 g) and imidazole (4.4 g) at 70°. After 5 days at this temperature, subsequent addition of *tert*-butylchlorodimethylsilane (6.5 g) and imidazole (4.4 g) was necessary. The solution was stirred for a further 2 days at 70° and then evaporated. The resulting syrup was dissolved in CH_2Cl_2 (50 mL) and water (50 mL). The aqueous layer was washed with CH_2Cl_2 (50 mL) and the organic layers were then washed with water (2 × 25 mL), dried (Na_2SO_4), and evaporated to a syrup that was eluted from a column of silica gel with EtOAc to yield **11** (6.8 g, 67.6%); ^{1}H-n.m.r. data (CCl_4): δ 6.0 (d, 1 H, H-1), 5.3 (t, 1 H, H-3), 4.0–3.0 (12 H), 2.0 (s, 3 H, 1 Ac), 1.4–1.2 (12 H, 4 Me), 1.2–0.9 (27 H, 3 Bu), and 0.2–0.0 (18 H, 6 Me).

Anal. Calc. for $C_{38}H_{74}O_{12}Si_3$: C, 56.54; H, 9.24; Si, 10.44. Found: C, 55.61; H, 8.77; Si, 8.61.

*3',4',6'-Tri-O-*tert*-butyldimethylsilyl-1',2:4,6-di-O-isopropylidenesucrose* (**12**). — To a solution of **11** (6.8 g) in dry MeOH (100 mL) was added M methanolic NaOMe (5 mL). The solution was stirred at room temperature for 3 days, and then made neutral with Amberlite IR-120 (H^+) resin. The resin was filtered off and the filtrate evaporated to give **12** (6.16 g, 95%), m.p. 203–206° (from MeOH), $[\alpha]_D$ +9.0° (*c* 2.1, Me_2CO); lit.[5] m.p. 206–209° (from MeOH), $[\alpha]_D$ +9.5° (*c* 2.0, Me_2CO).

*3',4',6'-Tri-O-*tert*-butyldimethylsilyl-1',2:4,6-di-O-isopropylidene-3-O-imidazolylthiocarbonylsucrose* (**13**). — A solution of **12** (6.16 g) and thiocarbonyldiimidazole (3 g) in dry 1,2-dichloroethane (70 mL) was boiled under reflux. Subsequent additions of thiocarbonyldiimidazole (3 × 1.5 g) after 29, 72, and 77 h were necessary. The reaction was complete in 3 days. The solution was evaporated and the residue was dissolved in CH_2Cl_2 (50 mL). The solution was washed with M HCl (50 mL), saturated aq. $NaHCO_3$ (50 mL) and water (50 mL), dried (Na_2SO_4) and evaporated. The resulting foam was eluted from a column of silica gel with ether to give **13** (4.76 g, 67%), $[\alpha]_D$ +17.8° (*c* 0.92, $CHCl_3$); ^{1}H-n.m.r. data (CCl_4): δ 8.0–

6.9 (3 s, 3 H, Im.), 6.0 (2 H, H-1,3), 4.03.0 (12 H), 1.15–1.5 (4 Me), 1.0–0.6 (27 H, 3 Bu), and 0.3–0.0 (18 H, 6 Me).

Anal. Calc. for $C_{40}H_{74}N_2O_{11}S\,Si_3$: C, 54.85; H, 8.52; N, 3.20; S, 3.66; Si, 9.63. Found: C, 53.94; H, 8.20; N, 3.28; S, 3.74; Si, 9.85.

*3',4',6'-Tri-*O*-*tert*-butyldimethylsilyl-3-deoxy-1',2:4,6-di-*O*-isopropylidene-sucrose* (**14**). — A solution of **13** (5.1 g) in dry PhMe (100 mL) was added, under N_2, to a refluxing solution of Bu_3SnH (1.6 mL) in PhMe (100 mL) during 1 h. A subsequent addition of Bu_3SnH (1.6 mL) after 2 h was necessary. The reaction was complete in 3 h. The solution was then evaporated and the residue dissolved in CH_2Cl_2 (100 mL). The solution was washed with water (2 × 100 mL), dried (Na_2SO_4) and evaporated. The resulting syrup was eluted from a column of silica gel with 3:1 hexane–ether to give **14** (3.3 g, 75.5%), $[\alpha]_D$ +6.5° (*c* 2.1, Me_2CO); lit.[5] $[\alpha]_D$ +6.37° (*c* 2.0, Me_2CO); ^{1}H-N.m.r. data (CCl_4): δ 5.9 (d, 1 H, H-1), 4.1–3.1 (13 H), 1.95–1.6 (2 H, H-3), 1.55–1.15 (2 s, 12 H, 4 Me), 1.05–0.65 (27 H, 3 Bu), and 0.3–0.0 (18 H, 6 Me).

3-Deoxysucrose (**15**). — A solution of **14** (2.15 g) in MeCN (50 mL) was stirred with $Bu_4NCl\cdot 2\,H_2O$ (0.25 g) and KF (2 g) for 48 h at 70°. The solution was then evaporated and the resulting syrup was dissolved in tetrahydrofuran (5 mL), AcOH (3 mL), and water (2 mL). The mixture was stirred at room temperature for 4 days, and then evaporated. The resulting foam was dissolved in water (10 mL) and the solution was evaporated. EtOH (10 mL) was added and removed by evaporation to give **15** (0.82 g, 87.5%), m.p. 145–150° (from EtOH), $[\alpha]_D$ +56° (*c* 1.0, H_2O); lit.[5] m.p. 185°, $[\alpha]_D$ +47° (*c* 1.33, water). ^{1}H-N.m.r. data (D_2O): δ 5.23 (d, 1 H, H-1), 4.18 (d, 1 H, H-3'), 4.0 (t, 1 H, H-4'), 3.84–3.47 (10 H), 2.08 (d, 1 H, H-3a), and 1.75 (dd, 1 H, H-3b).

Anal. Calc. for $C_{12}H_{22}O_{10}$: C, 44.17; H, 6.79. Found: C, 44.32; H, 6.75.

*1,3,4,6-Tetra-*O*-acetyl-β-*D*-fructofuranosyl 2,3-di-*O*-acetyl-4,6-di-*S*-(2-pyridyl)-4,6-dithio-α-*D*-galactopyranoside* (**16**). — A solution of **3** (8.1 g) in pyridine (80 mL) was stirred with 2,2'-dipyridyldisulfide (13.3 g) and Bu_3P (16.8 mL) for 48 h at room temperature. After evaporation, the resulting syrup was purified by column chromatography with 4:1 EtOAc–hexane (4:1) to give **16** (8.4 g, 79%) as a white foam, $[\alpha]_D$ −30° (*c* 1.0, CH_2Cl_2); ^{1}H-n.m.r. data (C_6D_6): δ 8.3–8.1 (2 m, 2 H, H-α), 7.0–6.25 (m, 6 H, H-β,β',γ), 6.08 (dd, 1 H, $J_{3,4}$ 4.15 Hz, H-3), 6.00 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.85–5.78 (m, 2 H, H-4, 2), 5.21 (m, 1 H, H-5), 4.67–4.36 (m, 7 H, H-3',4',5',6'a,6'b,1'a,1'b), 4.14–4.07 (m, 1 H, H-6a), 3.81–3.74 (m, 1 H, H-6b), and 1.97–1.40 (6 s, 18 H, 6 Ac).

Anal. Calc. for $C_{34}H_{40}N_2O_{15}S_2$: C, 52.30; H, 5.16; O, 30.74; N, 3.59; S, 8.21. Found: C, 51.77; H, 5.18; O, 31.02; N, 3.64; S, 8.39.

4,6-Dideoxysucrose (**17**). — A solution of **16** (5 g) in EtOH (80 mL) was vigorously stirred with freshly prepared Raney nickel[11] W4 (30 g) at room temperature for 3 h. After filtration and solvent evaporation the residue was dissolved in dry MeOH (20 mL) and treated with M methanolic NaOMe (2 mL). 4,6-Dideoxysucrose (**17**) crystallised during the reaction (1.04 g, 52%), m.p. 188°, $[\alpha]_D$ +56.6°

(*c* 1.2, H_2O); ^{1}H-n.m.r. data (D_2O): δ 5.36 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.22 (d, 1 H, $J_{3',4'}$ 8.6 Hz, H-3′), 4.07 (t, 1 H, H-4′), 4.0–3.6 (m, 7 H, H-3.5,1′a,1′b,5′,6′a,6′b), 3.46 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 2.08 (dd, 1 H, H-4*e*), 1.37 (q, 1 H, H-4*a*), and 1.21 (d, 3 H, Me-6).

Anal. Calc. for $C_{12}H_{22}O_9$: C, 46.45; H, 7.15; O, 46.40. Found: C, 46.45; H, 7.10; O, 46.28.

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