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Synthesis of a trehalose homolog, 6-deoxy-*α*-D-*gluco*-heptopyranosyl 6-deoxy-*α*-D-*gluco*-heptopyranoside, and the corresponding bis(heptosiduronic acid)

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ABSTRACT

Crystalline 6-deoxy-*α*-D-*gluco*-heptopyranosyl 6-deoxy-*α*-D-*gluco*-heptopyranoside (**8**) and (6-deoxy-*α*-D-*gluco*-heptopyranosyluronic acid) 6-deoxy-*α*-D-*gluco*-heptopyranosiduronic acid (**7**) were synthesized from *α,α*-trehalose (**1**). Reaction of 2,3,4,2′,3′,4′-hexa-*O*-acetyl-6,6′-di-*O*-tosyl-*α,α*-trehalose with sodium dicarbonylcyclopentadienyliron, followed by oxidative hydrolysis or methanolysis, gave the 2,3,4,2′,3′,4′-hexa-acetate of **7** or its dimethyl ester, respectively. *O*-Deacetylation (Zemplén) then gave **7** and its dimethyl ester. Reduction of the hexa-*O*-acetyldicarboxylic acid with borane–oxolane complex yielded **8**. Alternatively, cyanide displacement of hexa-*O*-acetyl-*α,α*-trehalose 6,6′-ditriflate gave the dinitrile hexa-acetate of **7**, which was *O*-deacetylated and then hydrolyzed with alkaline hydrogen peroxide to yield **7**. 2,3,4,2′,3′,4′-Hexa-*O*-benzyl-*α,α*-trehalose 6,6′-ditriflate was similarly converted into the dinitrile, which was hydrolyzed to the corresponding diamide. Treatment of the 2,3,4,2′,3′,4′-hexa-*O*-acetyl-*α,α*-trehalosuronic acid **16** with thionyl chloride followed by diazomethane gave a crystalline bisdiazoketone which, however, failed to produce the expected bis(heptosiduronic acid) on attempted Wolff rearrangement.

INTRODUCTION

In the context of ongoing projects[1] on the synthesis of new derivatives and analogs of *α,α*-trehalose (**1**), 6-deoxy-*α*-D-*gluco*-heptopyranosyl 6-deoxy-*α*-D-*gluco*-heptopyranoside (**8**) and the corresponding bis(heptosiduronic acid) **7** have been prepared. Novel types of analogs of the mycobacterial cord factor[2] of potential biological interest can be derived from these sugars. Three approaches to **7** and **8** were investigated.

RESULTS AND DISCUSSION

The first approach involved chain elongation by the ironcarbonyl chemistry previously elaborated[3] with monosaccharides. The known[4,5] 6,6′-di-*O*-tosyl-*α,α*-trehalose hexa-acetate (**2**) was reacted with sodium dicarbonylcyclopentadienyliron (NaFp) in oxolane, to form a sugar–iron intermediate (**3**) that was treated *in situ* with bromine and methanol to effect carbonyl insertion and methanolysis, and to yield 42% of methyl [(methyl 2,3,4-tri-*O*-acetyl-6-deoxy-*α*-D-*gluco*-heptopyranosyluronate) 2,3,4-tri-*O*-acetyl-6-deoxy-*α*-D-*gluco*-heptopyranosid]uronate (**4**). The yield was not as high as with

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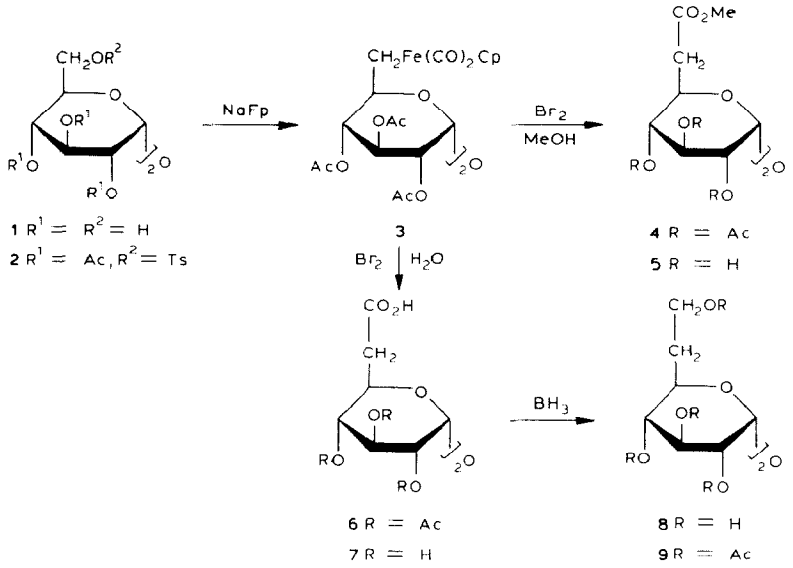
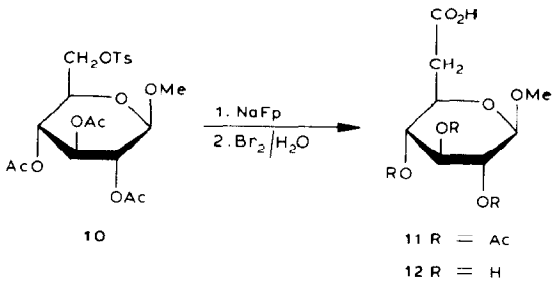
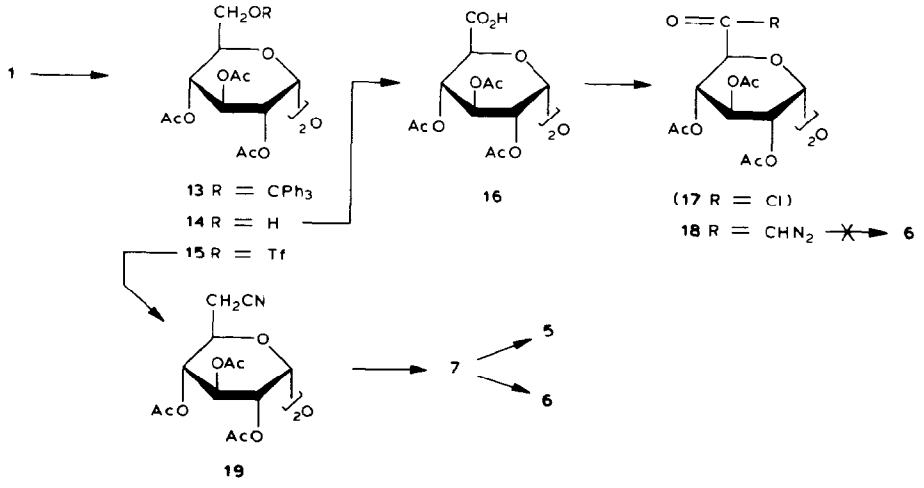


simpler substrates[3]. Zemplén *O*-deacetylation of **4** proceeded smoothly to give the diester **5**.

Attempted base-induced saponification of **4** gave (t.l.c.) a mixture of products possibly because of activation at C-6 by the methoxycarbonyl group and consequent *β*-elimination reactions. In order to circumvent this potential problem, the feasibility of preparing the acetylated diacid **6** by substituting water for methanol in the oxidative carbonyl insertion in **3** was investigated. Model experiments using methyl 2,3,4-tri-*O*-acetyl-6-*O*-tosyl-*β*-D-glucopyranoside (**10**) furnished methyl 2,3,4-tri-*O*-acetyl-6-deoxy-*β*-D-*gluco*-heptopyranosiduronic acid (**11**), but the yield (46%) was disappointing and did not match that (80%) achieved[3] in the synthesis of the methyl ester. However, alkaline hydrolysis of **11** readily provided the crystalline heptopyranosiduronic acid **12**. When applied to **3**, the procedure afforded 20–30% of crystalline **6**, saponification of which gave crystalline (6-deoxy-*α*-D-*gluco*-heptopyranosyluronic acid) 6-deoxy-*α*-D-*gluco*-heptopyranosiduronic acid (**7**).



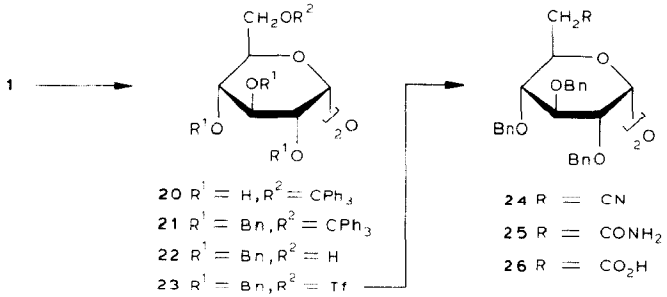


The application of Arndt–Eistert homologation[6] methodology to the acetylated trehalosuronic acid **16** was then examined. Compound **16** is available[7] by oxidation of 2,3,4,2′,3′,4′-hexa-*O*-acetyl-*α*,*α*-trehalose (**14**) with chromic acid, and **14** can be prepared[4,7] readily from **1** via the ditrityl ether **13**. Reaction of **16** with thionyl chloride, followed by treatment of the resulting acid chloride **17** (not characterized) with diazomethane, gave 65% of the crystalline diazoketone **18**. Unfortunately, attempted silver-catalyzed Wolff rearrangement[6] of **18** gave complex mixtures of products, and the approach was abandoned.

The hexa-acetate **14** was converted into the 6,6′-ditriflate **15** which, with potassium cyanide in aqueous acetonitrile, furnished the dinitrile hexa-acetate **19**. *O*-Deacetylation did not occur during this operation but was subsequently effected (Zemplén), and hydrolysis of the nitrile groups with aqueous alkali in the presence of hydrogen peroxide then gave **7**. Treatment of **7** with methanol–hydrogen chloride or diazomethane gave **5**, and acetylation of **7** produced **6**.

Treatment of the diacid hexa-acetate **6** with borane in oxolane reduced the carboxyl groups and caused partial deacetylation. Zemplén *O*-deacetylation of the product then furnished 6-deoxy-*α*-D-*gluco*-heptopyranosyl 6-deoxy-*α*-D-*gluco*-heptopyranoside (**8**), and reacetylation gave the octa-acetate **9**.

For future uses of **7** in synthesis, its hexa-*O*-benzyl derivative **26** was desired. Consequently, 2,3,4,2′,3′,4′-hexa-*O*-benzyl-*α*,*α*-trehalose[8] (**22**) was prepared from **1** *via* the trityl ethers **20** and **21**. The 6,6′-ditriflate (**23**) of **22** was treated with potassium cyanide to give the dinitrile **24**. Hydrolysis of **24** with sodium hydroxide and hydrogen peroxide at room temperature proceeded readily but stopped at the amide stage (in contrast to the hydrolysis of **19**), and 83% of the diamide **25** was isolated. Not only was **25** exceptionally resistant to further hydrolysis under a variety of alkaline conditions, but also it failed to undergo deamination with nitrous acid.



The c.i.-mass spectrum of the "homotrehalose" **8** contained a signal for $[M + H]^+$ at *m/z* 371, as the base peak, whereas such peaks were generally weak or absent in the spectra of the bis(heptosiduronic acid) derivatives **4**–**7** and **19**, and in that of the trehalose ditriflate **15**. However, intense peaks were present at *m/z* for $0.5[M - 16]^+$ (100% for c.i.-mass spectra; 50% for f.a.b.-mass spectra of **6** and **19**), which represented the glycosyl ion resulting from rupture of the disaccharidic bond. Little useful information could be derived from mass spectra of the benzylated compounds **21**–**25**.

EXPERIMENTAL

General methods. — Column chromatography was performed with silica gel (Merck 9385; 20–45 μm), using ethyl acetate–hexane *A*, 3:1; *B*, 2:1; *C*, 1.5:1; *D*, 1:1; *E*, 1:1.5; *F*, 1:2; and *G*, 1:3; water–methanol–ethyl acetate *H*, 4:5:10; *I*, 4:5:15; *J*, 4:5:20; and *K*, 4:5:30; *L*, 1:19 methanol–ethyl acetate; *M*, 1:19 methanol–chloroform; and ether–hexane *N*, 1:2; and *O*, 1:5. Melting points were determined in capillaries with a Gallenkamp apparatus. Optical rotations were measured at ~25°. I.r. data (ν_{max}) were obtained for all compounds described and were consistent with the assigned structures; only significant bands are reported. Mass spectra were obtained by the c.i. mode (ether or isobutane), and some by the f.a.b. mode using glycerol as the matrix. The ^{1}H- and ^{13}C-n.m.r. spectra were recorded for solutions in $CDCl_3$ unless otherwise stated; data recorded with a Varian Gemini 200 instrument are denoted as 200 and 50.29 MHz, respectively, whereas data without special notation refer to spectra at 300 and 75.43 MHz obtained with a Varian XL 300 instrument. Assignments of ^{13}C peaks were aided by ADEPT or APT experiments. The symmetrical disaccharide derivatives gave only one set of signals which, for convenience, are recorded with reference to one moiety.

*Methyl [(methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-*D*-gluco-heptopyranosyluronate) 2,3,4-tri-*O*-acetyl-6-deoxy-α-*D*-gluco-heptopyranosid]uronate* (**4**). — (*a*) *From* **2** *by the ironcarbonyl method.* 6,6′-Di-*O*-tosyl-α,α-trehalose hexa-acetate[5] (**2**) was reacted with 1.3 mol of sodium dicarbonyl-η^5-cyclopentadienyliron (NaFp) under the general condi-

tions detailed[3] for the reaction of **10**. A solution of 6 mmol of NaFp [prepared from 1.065 g of $Fe(CO)_2Cp$ dimer, and sodium amalgam from 6 mL of Hg and 1.5 g of Na] in oxolane (200 mL) was added under anhydrous conditions to **2** (2.025 g, 2.25 mmol) under N_2. Compound **2** dissolved on stirring and, after 1.5 h, was completely consumed [t.l.c. (solvent *B*) and charring with sulfuric acid] and a strong, faster-moving, yellow spot of the iron derivative **3** was seen prior to spraying, together with unidentified trace components. A stream of CO was passed through the solution at 0°, and absolute methanol (350 mL) was added, followed by Br_2 (2.1 mL). T.l.c. (solvent *B*) revealed the reaction to be complete after 0.5 h; the yellow spot of **3** (visible without spraying) was replaced by a strong spot of **4** (R_F 0.6) accompanied by faster- and slower-moving spots of by-products (visible after spraying and heating). The solution was concentrated to a small volume, diluted with ethyl acetate, washed sequentially with aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. The resulting brown syrup was dissolved in ether and reprecipitated with light petroleum (b.p. 35–60°). The supernatant solvent was decanted, and column chromatography (solvent *D*) of the oily precipitate gave **4** (620 mg, 42%), m.p. 135–137° (from methanol), $[\alpha]_D$ +146° (*c* 0.6, chloroform); ν_{max}^{Nujol} 1750 cm^{-1}. Mass spectrum (c.i.): *m/z* 331 (100%, $[0.5(M - 16)]^+$), 271 (10%, $[0.5(M - 16) - AcOH]^+$), 211 (25%, $[0.5(M - 16) + H - 2\ AcOH]^+$). N.m.r. data: ^1H, δ 5.50 (dd, $J_{3,4}$ 9.2, $J_{2,3}$ 10.0 Hz, H-3), 5.22 (d, $J_{1,2}$ 3.8 Hz, H-1), 5.17 (dd, $J_{1,2}$ 3.7, $J_{2,3}$ 10.2 Hz, H-2), 4.88 (dd, $J_{3,4}$ 9.2, $J_{4,5}$ 10.2 Hz, H-4), 4.34 (m, H-5), 3.62 (s, 3 H, OMe), 2.45 (m, 2 H, H-6,6'), 2.11, 2.02, and 2.00 (3 s, 3 H each, 3 OAc); ^{13}C, δ 170.1, 169.9, 169.7, 169.7 (CO), 90.8 (C-1), 71.8, 70.2, 68.9, and 66.3 (C-2,3,4,5), 52.0 (OMe), 36.6 (C-6), and 20.6 (*CO*Me).

Anal. Calc. for $C_{28}H_{38}O_{19}$ (678.6): C, 49.56; H, 5.64. Found: C, 49.36; H, 5.54.

(b) By acetylation of **5**. A solution of **5** (35 mg) in pyridine (4 mL) was treated overnight at 25° with acetic anhydride (1 mL) and 4-dimethylaminopyridine (3 mg). Formation of **4** (R_F 0.6) was indicated by t.l.c. (solvent *B*). Conventional processing gave **4** (31.5 mg, 64%), m.p. 134–135° (from methanol), $[\alpha]_D$ +144° (*c* 0.5, chloroform).

*Methyl [(methyl 6-deoxy-α-*D*-gluco-heptopyranosyluronate) 6-deoxy-α-*D*-gluco-*heptopyranosid]uronate (**5**). — (*a*) *From the hexa-acetate* **4**. To a solution of **4** (50 mg) in methanol (5 mL) was added 1 drop of methanolic M sodium methoxide at room temperature. Deacetylation was complete after 15 min as indicated by t.l.c. (R_F of **5**: 0.7 and 0.4 with solvents *H* and *J*, respectively). Deionization and concentration of the solution, followed by trituration of the residue with methanol–ether, gave **5** (29 mg, 92%) as a white solid that sintered near 90° and gradually turned into a viscous foam above 100°, $[\alpha]_D$ +138° (*c* 1.1, methanol). Mass spectrum (c.i.): *m/z* 205 (100%, $0.5[M - 16]^+$), 187 (56%, $0.5[M - 16 - H_2O]^+$), 169 (34%, $0.5[M - 16 - 2H_2O]^+$). N.m.r. data (D_2O): ^1H, δ 5.14 (d, $J_{1,2}$ 3.85 Hz, H-1), 4.17 (dt, $J_{5,6}$ 3, $J_{4,5} = J_{5,6'}$ = 9.9 Hz, H-5), 3.86 (t, $J_{2,3} \approx J_{3,4} \approx$ 9.5 Hz, H-3), 3.74 (s, 3 H, OMe), 3.70 (dd, $J_{1,2}$ 3.85, $J_{2,3}$ 9.9 Hz, H-2), 3.36 (t, $J_{3,4} \approx J_{4,5} \approx$ 9.5 Hz, H-4), 2.98 (dd, $J_{5,6}$ 3, $J_{6,6'}$ 15.9 Hz, H-6), 2.58 (dd, $J_{5,6'}$ 9.8, $J_{6,6'}$ 15.9 Hz, H-6'); ^{13}C (50.29 MHz), δ 177.2 (CO), 95.8 (C-1), 76.0, 75.3, 74.1, 71.8 (C-2,3,4,5), 55.5 (OMe), 39.5 (C-6).

Anal. Calc. for $C_{16}H_{26}O_{13}$ (426.4): C, 45.07; H, 6.15. Found: C, 45.18; H, 6.22.

(*b*) *From the dicarboxylic acid* **7**. A stream of HCl gas was passed under anhydrous conditions for a few seconds into a solution of **7** (74 mg) in methanol (15 mL). The solution was kept overnight at 23°, then concentrated with several additions of fresh methanol, and the residue (R_F 0.4, t.l.c. with solvent *J*) was crystallized from methanol–ether to give **5** (60 mg, 87%). Alternatively, a solution of **7** (30 mg) in aqueous methanol was treated with ethereal diazomethane until the yellow color persisted. Evaporation of the solvents and trituration of the residue with methanol–ether gave **5** (31.8 mg, 99%).

*(2,3,4-Tri-*O*-acetyl-6-deoxy-α-*D*-gluco-heptopyranosyluronic acid) 2,3,4-tri-*O*-acetyl-6-deoxy-α-*D*-gluco-heptopyranosiduronic acid* (**6**). — (*a*) *From* **2** *by the iron carbonyl method.* The procedure specified for synthesis of **4** was modified as follows. Ditosylate[5] **2** (1.62 g, 1.8 mmol) was reacted with a 3.3 mol excess of NaFp [from 2.13 g of $Fe(CO)_2Cp$ dimer, 12 mmol] in oxolane (60 mL) during 70 min. T.l.c. (solvent *D*) revealed no **2** but a faster-moving, yellow spot (visible without spraying) of the sugar–iron intermediate. A stream of CO was passed through the solution at 0°, and water (60 mL) followed by Br_2 (2 mL) was added. After 10 min, the solution was concentrated to a small volume, and extracted repeatedly with ethyl acetate, and the combined extracts were washed with water, dried ($MgSO_4$), and concentrated. Column chromatography ($CHCl_3$, then with added methanol up to 2%) of the dark residue gave **6**, isolated as a yellow oil (1.35 g). Crystallization from ethyl acetate–light petroleum, after treatment with activated charcoal, and 3 recrystallizations from ethyl acetate–hexane gave colorless **6** (304 mg, 26%), which sintered at ~ 50° and melted indistinctly at 75–95°, $[\alpha]_D$ +112° (*c* 0.5, chloroform). Mass spectrum (+ve f.a.b.): *m/z* 651 (6%, $[M + 1]^+$), 317 (51%, 0.5$[M - 16]^+$). N.m.r. data: ^1H, δ 5.49 (dd, $J_{2,3}$ 10, $J_{3,4}$ 9.2 Hz, H-3), 5.19 (dd, $J_{1,2}$ 3.8, $J_{2,3}$ 10 Hz, H-2), 5.09 (d, $J_{1,2}$ 3.8 Hz, H-1), 4.86 (t, $J_{3,4} \approx J_{4,5} \approx$ 10Hz, H-4), 4.33 (dt, H-5), 2.50 (m, 2 H, H-6,6'), 2.03, 2.01, and 1.99 (3 s, 3 H each, 3 OAc); ^{13}C, δ 176.1 (CO_2H), 169.8, 169.7, 169.4 (*Me*CO), 90.6 (C-1), 71.5, 70.3, 69.0, 65.8 (C-2,3,4,5), 36.2 (C-6), 20.8, 20.8, 20.7 (*C*OMe).

Anal. Calc. for $C_{36}H_{34}O_{19}$ (650.5): C, 48.00; H, 5.27. Found: C, 48.19; H, 5.43.

(*b*) *From the dicarboxylic acid* **7** *by acetylation.* To a solution of **7** (125 mg) in glacial acetic acid (3 mL) and $CHCl_3$ (1 mL) containing a catalytic amount of 4-dimethylaminopyridine was added acetyl chloride (1 mL). Formation of **6** (R_F 0.6) was complete after 1 h (t.l.c., solvent *I*). A minor precipitate was removed, and the filtrate was concentrated with addition of toluene and then ethanol. A solution of the light-brown residue in $CHCl_3$ was washed twice with water, dried ($MgSO_4$), and concentrated. Flash chromatography ($CHCl_3$, then solvent *M*) of the foamy residue (177 mg, 86%) on silica gel (4 g) and crystallization from ethyl acetate–hexane gave **6** (134 mg, 65%), $[\alpha]_D$ +113° (*c* 0.7, chloroform).

Acetylation of **7** with acetic anhydride in the presence of conc. H_2SO_4 gave crystalline **6** in low yield only (28%).

*(6-Deoxy-α-*D*-gluco-heptopyranosyluronic acid) 6-deoxy-α-*D*-gluco-heptopyranosiduronic acid* (**7**). — (*a*) *From the hexa-acetate* **6**. Compound **6** (85 mg) was deacetylated at room temperature in methanol (4 mL) made alkaline (pH 9) with sodium methoxide. Deionization with Amberlite IR-120 (H^+) resin after 30 min and concentration of the solution gave colorless **7**, R_F 0.4 (t.l.c., solvent *H*), which crystallized on trituration with a little methanol and ethyl acetate. The white, somewhat hygroscopic powder (44 mg, 84%) had no distinct melting point but began to sinter near 60° and turned gradually into a glassy foam on heating above 90°; $[\alpha]_D$ +144° (*c* 1.6, water); ν_{max}^{Nujol} 3400–3100, 2600, 1710 cm^{-1}. Mass spectrum (+ve f.a.b.): *m/z* 399 (7%, $[M + 1]^+$); *m/z* (−ve f.a.b.) 397 (44%, $[M - 1]^-$; *m/z* (c.i.) 381, 363, and 345 (9, 2, and 4%, $[M + 1 - 1, 2$, and $3H_2O]^+$), 265 (23%), 191 (100%, $0.5[M - 16]^+$), 173 (56%, $[0.5(M - 16) - H_2O]^+$), 155 (22%, $[0.5(M - 16) - 2H_2O]^+$). N.m.r. data (D_2O): ^1H, δ 5.20 (d, $J_{1,2}$ 3.85 Hz, H-1), 4.16 (dt, $J_{5,6}$ 2.9, $J_{4,5} = J_{5,6'}$ = 9.9 Hz, H-5), 3.88 (dd, $J_{3,4}$ 9.0, $J_{2,3}$ 9.9 Hz, H-3), 3.70 (dd, $J_{1,2}$ 3.9, $J_{2,3}$ 9.9 Hz, H-2), 3.35 (dd, $J_{3,4}$ 9, $J_{4,5}$ 9.9 Hz, H-4), 2.97 (dd, $J_{5,6}$ 2.9. $J_{6,6'}$ 15.8 Hz, H-6), 2.52 (dd, $J_{5,6'}$ 15.8 Hz, H-6′); ^{13}C (50.29 MHz), δ 176.6 (CO_2H), 93.6 (C-1), 74.0, 73.4, 72.1, 69.7 (C-2,3,4,5), 37.6 (C-6).

Anal. Calc. for $C_{14}H_{22}O_{13}$ (398.3): C, 42.21; H, 5.57. Found: C, 41.89; H, 5.65.

(*b*) *From the dinitrile* **19**. A solution of **19** (1.145 g) in methanol (20 mL) was made alkaline (pH 9) by dropwise addition of methanolic sodium methoxide, to effect *O*-deacetylation which was complete after 20 min, as indicated by the appearance of a single new spot (R_F 0.73) in t.l.c. (solvent *H*). The solution was concentrated to a syrup which, together with powdered NaOH (340 mg), was dissolved in aqueous 25% H_2O_2 (12 mL). The mixture was stored at room temperature without agitation and, when the effervescence ceased, more 25% H_2O_2 (5 mL) and NaOH (135 mg) were added. This procedure was repeated three times in the course of 4 days. Monitoring of the reaction by t.l.c. (solvent *H*) revealed the slow formation of slow-moving **7** together with products of intermediate mobilities, which gradually disappeared again; eventually, a single spot of **7** remained, R_F 0.4 (triple irrigation). When the reaction mixture was stirred, the rate *decreased* and completion was then attained only after 1.5–2 weeks. The solution was deionized with Amberlite IR-120 (H^+) resin, filtered, boiled for 3 h in order to decompose H_2O_2, and concentrated to dryness to give **7** as a white, hygroscopic powder (723 mg, 97%). Crystallization from methanol–ethyl acetate furnished **7** (666 mg, 89.5%), $[\alpha]_D$ +130° (*c* 0.7, water).

*6-Deoxy-α-*D*-gluco-heptopyranosyl 6-deoxy-α-*D*-gluco-heptopyranoside* (**8**). — A solution of **6** (54 mg, 0.083 mmol) in oxolane (1.8 mL) containing 0.8 mmol of BH_3 was stirred under N_2 for 2 h at room temperature and then for 40 min at the reflux temperature. T.l.c. (solvent *I*) revealed several spots attributable to partially deacetylated reduction products. The excess of reductant was decomposed by continued heating (10 min) with added methanol, the solvents were evaporated, and the residue was treated with sodium methoxide in methanol at pH 9 and ~23° for 15 min, which effected complete deacetylation. T.l.c. (solvent *I*) then showed a single spot (R_F 0.3). Upon deionization with Amberlite IR-120 (H^+) resin and concentration of the solution, **8** was

obtained as a colorless syrup (29 mg, 94%), the ^{13}C-n.m.r. spectrum of which agreed with the structure. Crystallization from methanol–acetone gave a material with m.p. 201°, $[\alpha]_D$ +183° (*c* 1.2, water). Mass spectrum (c.i.): *m/z* 371 (100%, $[M + 1]^+$), 177 (27%, 0.5$[M - 16]^+$), 159 (83%, $[0.5(M - 16) - H_2O]^+$. N.m.r. data (D_2O): ^1H (200 MHz), δ 5.10 ($J_{1,2}$ 3.8 Hz, H-1), 3.78–3.71 (m, **4** H, unresolved), 3.64 (dd, $J_{1,2}$ 3.8, $J_{2,3}$ 9.9 Hz, H-2), 3.27 (dd, *J* 9.0 and 9.7 Hz), 2.09 and 1.69 (2 m, 1 H each, H-6,6′); ^{13}C (50.29 MHz), δ 95.85 (C-1), 76.0, 75.1, 73.6, 71.3 (C-2,3,4,5), 60.75 (C-7), 35.6 (C-6).

Anal. Calc. for $C_{14}H_{26}O_{11}$ (370.4): C, 45.40; H, 7.08. Found: C, 45.37; H, 7.05.

A solution of syrupy **8** (19 mg) in a few drops of *N,N*-dimethylformamide was acetylated overnight at ~23° with 1:1 acetic anhydride–pyridine (1 mL). Removal of the reagent by co-evaporation with excess of toluene gave the syrupy octa-acetate **9**. N.m.r. data: ^1H (200 MHz), δ 5.42, (dd, *J* 9.3 and 10 Hz, H-3 or H-4), 5.21 (d, $J_{1,2}$ 3.95 Hz, H-1), 4.97 (dd, $J_{1,2}$ 3.85, $J_{2,3}$ 10.1 Hz, H-2), 4.88 (dd, *J* 9.3 and 10 Hz, H-4 or H-3), 4.08 (octet, 2 H, *W* 44 Hz, H-7,7′), 3.82 (octet, *J* 5, 7, and 10 Hz, H-5), 2.10, 2.01, 2.00, 1.99 (4 s, 3 H each, 4 AcO), 1.75 (m, 2 H, H-6,6′); ^{13}C (75.43 MHz), δ 170.7, 169.8, 169.6, 169.5 (*Me*CO), 90.8 (C-1), 72.0, 70.2, 70.1, 66.9 (C-2,3,4,5), 60.2 (C-7), 30.4 (C-4), 20.9, 29.75, 20.75, 20.7 (*CO*Me).

*Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-*D-gluco-*heptopyranosiduronic acid* (**11**). — Glycoside[3] **10** (1.42 g, 3 mmol) was treated with NaFp (4 mmol) in oxolane (40 mL), as described[3] for the preparation of the methyl ester of **11**, except that *water* (30 mL) and Br_2 (1.4 mL) were used in the step of oxidative carbonyl insertion. The latter step was complete after a few minutes (t.l.c., solvent *D*). In the work-up procedure[3], washing of the ethyl acetate solution of the crude products with aqueous $NaHCO_3$ was omitted and flash chromatography was performed with solvent *F*. Compound **11** (R_F 0.45, solvent *K*) was obtained as a syrup that crystallized from ethyl acetate–hexane to give 483 mg (46.3%) of pure material, m.p. 167–168°, $[\alpha]_D$ −12° (*c* 0.7, chloroform). Mass spectrum (c.i.): *m/z* 317 (98%, $[M - OMe]^+$), 289 (22%, $[M - OAc]^+$), 257 (21%, $[M - OMe - AcOH]^+$), 229 (7.5%, $[M + 1 - 2\,AcOH]^+$). N.m.r. data: ^1H, δ 5.18 (~t, $J_{2,3} \approx J_{3,4} \approx$ 9.5 Hz, H-3), 4.94 (dd, $J_{1,2}$ 7.9, $J_{2,3}$ 9.7 Hz, H-2), 4.90 (dd, $J_{3,4}$ 9.5, $J_{4,5}$ 10 Hz, H-4), 4.33 (d, $J_{1,2}$ 7.9 Hz, H-1), 3.93 (ddd, $J_{5,6}$ 4.8, $J_{5,6'}$ 7.7, $J_{4,5}$ 10 Hz, H-5), 3.45 (s, 3 H, OMe), 2.59 (m, 2 H, H-6,6′), 2.03, 2.01, and 1.98 (3 s, 3 H each, 3 OAc); ^{13}C, δ 175.3 (CO_2H), 170.1, 169.5, 169.3 (*Me*CO), 101.5 (C-1), 72.8, 71.5, 71.4, 70.0 (C-2,3,4,5), 57.0 (OMe), 36.7 (C-6), 20.8, 20.7, 20.7 (*CO*Me).

Anal. Calc. for $C_{14}H_{20}O_{10}$ (348.3): C, 48.27; H, 5.79. Found: C, 48.05; H, 5.87.

*Methyl 6-deoxy-β-*D-gluco-*heptopyranosiduronic acid* (**12**). — The triacetate **11** (100 mg) was treated with methanolic 0.05M sodium methoxide (10 mL) during 1 h. Deionization with Amberlite IR-120 (H^+) resin and concentration of the solution gave a colorless syrup that crystallized from methanol–ethyl acetate to afford **12** (59 mg, 92.5%), m.p. 172–173°, $[\alpha]_D$ −20° (*c* 0.45, methanol). N.m.r. data (D_2O): ^1H (200 MHz), δ 4.42 (d, $J_{1,2}$ 8 Hz, H-1), 3.83 (dt, $J_{5,6}$ 3.1, $J_{4,5} = J_{5,6'} = 9.6$ Hz, H-5), 3.56 (s, 3 H, OMe), 3.5–3.3 (m, 3 H, H-2,3,4), 2.99 (dd, $J_{5,6}$ 3.1, $J_{6,6'}$ 15.9 Hz, H-6), 2.55 (dd, $J_{5,6'}$ 9.7, $J_{6,6'}$ 15.9 Hz, H-6′); ^{13}C (50.29 MHz), δ 178.6 (CO_2H), 106.3 (C-1), 78.6, 76.2, 75.9, 75.3 (C-2,3,4,5), 60.1 (OMe), and 39.7 (C-6).

Anal. Calc. for $C_8H_{14}O_7$ (222.2): C, 43.24; H, 6.35. Found: C, 43.16; H, 6.38.

*2,3,4,2',3',4'-Hexa-*O*-acetyl-6,6'-di-*O*-trityl-α,α-trehalose* (**13**). — Prepared according to Liav and Goren[7], **13** had m.p. 241°, $[\alpha]_D$ +110° (*c* 0.6, chloroform); lit.[7] m.p. 238–241°, $[\alpha]_D$ + 112.3°. ^{1}H-N.m.r. data: δ 7.38 and 7.24 (2 m, Ph), 5.44 (d, $J_{1,2}$ 3.7 Hz, H-1), 5.43 (dd, $J_{3,4}$ 9.3, $J_{2,3}$ 10.4 Hz, H-3), 5.17 (dd, $J_{1,2}$ 3.8, $J_{2,3}$ 10.3 Hz, H-2), 5.12 (dd, $J_{3,4}$ 9.3, $J_{4,5}$ 10.5 Hz, H-4), 4.10 (dt, $J_{5,6} = J_{5,6'} = 3.5$, $J_{4,5}$ 10.3 Hz, H-5), 3.08 (d, 2 H, *J* 3.5 Hz, H-6,6'), 1.97, 1.87, 1.73 (3 s, 3 H each, 3 OAc).

*2,3,4,2',3',4'-Hexa-*O*-acetyl-α,α-trehalose* (**14**). — Compound **13** (36 g) was detritylated with aqueous 80% acetic acid (600 mL) by stirring the suspension for 1.5 h at 75°, as described[7]. The mixture was concentrated to half its volume, filtered from precipitated triphenylmethanol, and brought to dryness by concentration with toluene and ethanol. Crystallization of the residue from oxolane–hexane gave **14** (13.8 g), and flash chromatography (solvent *B*) of the material in the mother liquor on silica gel (190 g) gave more **14** (1.1 g; total yield, 75%), m.p. 84°; lit.[7] m.p. 82–86°. ^{1}H-N.m.r. data: δ 5.51 (dd, $J_{3,4}$ 9.4, $J_{2,3}$ 10.3 Hz, H-3), 5.28 (d, $J_{1,2}$ 3.9 Hz, H-1), 4.99 (dd, $J_{3,3}$ 9.4, $J_{4,5}$ 10.4 Hz, H-4), 4.96 (dd, $J_{1,2}$ 4, $J_{2,3}$ 10.3 Hz, H-2), 3.93 (m, H-5), 3.62 (m, H-6,6'), 2.07, 2.06, 2.02 (3 s, 3 H each, 3 OAc).

*2,3,4,2',3',4'-Hexa-*O*-acetyl-6,6'-di-*O*-(trifluoromethyl)sulfonyl-α,α-trehalose* (**15**). — To a mixture of dry 1,2-dichloroethane (200 mL, freshly distilled from P_2O_5) and dry pyridine (18.6 mL) at −15° was added, dropwise, trifluoromethanesulfonic anhydride (15.5 mL) under N_2. The mixture was stirred for 10 min and a solution of **14** (13.63 g) in dry 1,2-dichloroethane (30 mL) was added dropwise. The conversion of **14** (R_F 0.3) into **15** (R_F 0.65) was complete after 15 min (t.l.c., solvent *A*). The mixture was extracted twice with aqueous 5% HCl, washed with aqueous $NaHCO_3$ and then water, dried ($MgSO_4$), and concentrated. Trituration of the oil with anhydrous ether gave **15** as a white solid (15.59 g, 79%) which decomposed without melting; $[\alpha]_D$ +104° (*c* 0.6, chloroform). Mass spectrum (c.i.): *m/z* 799 (2.4%, [M + 1−AcOH]$^+$), 709 (2.1%, [M + 1−TfOH]$^+$), 421 (96%, 0.5[M − 16]$^+$). N.m.r. data: ^{1}H, δ 5.47 (dd, $J_{3,4}$ 9.25, $J_{2,3}$ 10.35 Hz, H-3). 5.28 (d, $J_{1,2}$ 3.85 Hz, H-1), 5.09 (dd, $J_{1,2}$ 3.85, $J_{2,3}$ 10.3 Hz, H-2), 4.98 (dd, $J_{3,4}$ 9.2, $J_{4,5}$ 10.4 Hz, H-4), 4.50 (dd, $J_{5,6}$ 6.5, $J_{6,6'}$ 11.5 Hz, H-6), 4.39 (dd, $J_{5,6'}$ 2.5, $J_{6,6'}$ 11.5 Hz, H-6'), 4.24 (m, H-5), 2.08, 2.06, 2.02 (3 s, 3 H each, 3 OAc); ^{13}C, δ 169.7, 169.3, 169.0 (*Me*CO), 93.3 (C-1), 73.3 (C-6), 69.5, 69.2, 68.3, 68.1 (C-2,3,4,5), 20.7, 20.6, 20.5 (*CO*Me).

Anal. Calc. for $C_{26}H_{32}F_6O_{21}S_2$ (858.6): C, 36.37; H, 3.76; S, 7.47. Found: C, 36.24; H, 3.92; S, 7.68.

*(2,3,4-Tri-*O*-acetyl-α-*D*-glucopyranosyluronic acid) 2,3,4-tri-*O*-acetyl-α-*D*-glucopyranosiduronic acid* (**16**). — Prepared from **14** by oxidation with Jones reagent essentially as described[7], and crystallized from chloroform–light petroleum, **16** had m.p. 175–179°, $[\alpha]_d$ +168° (*c* 0.5, chloroform); lit.[7] m.p. 143–145° (from ether–hexane), $[\alpha]_D$ +157°; lit.[9] m.p. 166–170°, $[\alpha]_D$ +151°. ^{1}H-N.m.r. data: δ 5.51 (dd, $J_{2,3}$ 10, $J_{3,4}$ 9.5 Hz, H-2), 5.33 (d, $J_{1,2}$ 3.8 Hz, H-1), 5.24 (dd, $J_{3,4}$ 9.4, $J_{4,5}$ 10.2 Hz, H-4), 5.09 (dd, $J_{1,2}$ 3.8, $J_{2,3}$ 10 Hz, H-2), 4.48 (d, $J_{4,5}$ 10.2 Hz, H-5), 2.08, 2.06, 2.04 (3 s, 3 H each, 3 OAc).

2,3,4-Tri-O-*acetyl-7-diazo-7-deoxy-α*-D-gluco-*heptopyranosyl-6-ulose-2,3,4-tri*-O-*acetyl-7-7-diazo-7-deoxy-α*-D-gluco-*heptopyranosid-6-ulose* (**18**). — A solution of **16** (0.20 g) in benzene (10 mL) containing one drop each of triethylamine and *N,N*-dimethylformamide was treated at ~25° with freshly distilled $SOCl_2$ (0.15 mL). After 16 h, the solvent was evaporated and two portions of benzene were evaporated from the residue **17**, to a solution of which in benzene (5 mL) at 5° was added ice-cold ethereal (10 mL) diazomethane (from 0.5 g of *N*-nitrosomethylurea). The mixture was kept at ambient temperature, and the formation of **18** (R_F 0.3, t.l.c. with solvent *C*) was complete after 1 h. The solvent was evaporated and replaced by CH_2Cl_2 (1.5 mL) for separation of **18** from by-products on a chromatotron (solvent *E*). The oily **18** obtained upon concentration of the appropriate effluent fractions crystallized on trituration with ether to yield material (141 mg, 65%) having m.p. 169–170°, $[\alpha]_D$ +193° (*c* 0.5, chloroform); ν_{max}^{Nujol} 2110, 1750, 1640, 1370, 1215, 1040 cm^{-1}. N.m.r. data: ^1H, δ 5.61 (s, H-7), 5.50 (dd, $J_{3,4}$ 9.6, $J_{2,3}$ 10.2 Hz, H-3, 5.29 (d, $J_{1,2}$ 3.9 Hz, H-1), 5.09 (t, $J_{3,4} \approx J_{4,5} \approx 9.7$ Hz, H-4), 4.96 (dd, $J_{1,2}$ 4, $J_{2,3}$ 10.2 Hz, H-2), 4.24 (d, $J_{4,5}$ 10.1 Hz, H-5), 2.08, 2.05, 2.02 (3 s, 3 H each, 3 OAc); ^{13}C, δ 188.2 (C-6), 170.0, 169.6, 169.4 (*Me*CO), 93.5 (C-1), 72.6, 69.7, 69.4, 69.2 (C-2,3,4,5), 54.1 (C-7), 20.7, 20.65, 20.6 (*CO*Me).

2,3,4-Tri-O-*acetyl-6-deoxy-α*-D-gluco-*heptopyranosylurononitrile 2,3,4-tri*-O-*acetyl-6-deoxy-α*-D-gluco-*heptopyranosidurononitrile* (**19**). — A mixture of **15** (15.5 g), acetonitrile (180 mL), water (20 mL), and KCN (3.1 g) was stirred at ~25° for 2 h. The formation of **19** was indicated in t.l.c. (solvent *A*) by a spot having an R_F value (0.62) marginally lower than that of **15**. After concentration, the oily residue was partitioned between CH_2Cl_2 and water. The organic phase was washed twice with water, dried ($MgSO_4$), and concentrated, to give crude **19** as a brown syrup. Flash chromatography (190 g of silica gel; solvent *D*) and crystallization from methanol gave **19** as a colorless solid (8.95 g, 81%) which sintered at 85° and melted indistinctly at 95–110°; $[\alpha]_D$ +129° (*c* 0.5, chloroform); ν_{max}^{Nujol} 2250 (weak but sharp, CN), 1750 (strong) cm^{-1}. Mass spectra: *m/z* (+ve f.a.b.) 613 (1%, $[M + 1]^+$), 298 (49%, $0.5[M - 16]^+$); *m/z* (c.i.) 612 (1.4%, M^+), 553 (1.2%, $[M + 1 - AcOH]^+$), 298 (100%, $0.5[M - 16]^+$). N.m.r. data: ^1H, δ 5.46 (dd, $J_{3,4}$ 9.3, $J_{2,3}$ 10.2 Hz, H-3), 5.31 (d, $J_{1,2}$ 3.9 Hz, H-1), 5.09 (dd, $J_{1,2}$ 3.9, $J_{2,3}$ 10.25 Hz, H-2), 4.93 (dd, $J_{3,4}$ 9.3, $J_{4,5}$ 9.9 Hz, H-4), 4.16 (dt, $J_{5,6} = J_{5,6'} = 6.1$, $J_{4,5}$ 10 Hz, H-5), 2.55 (d, 2 H, H-6,6'), 2.14, 2.10, 2.02 (3 s, 3 H each, 3 OAc); ^{13}C, δ 169.7, 169.6, 169.3 (*Me*CO), 115.6 (CN), 93.1 (C-1), 71.6, 69.5, 69.4, 66.3 (C-2,3,4,5), 21.0 (C-6), 20.8, 20.75, 20.7 (*CO*Me).

Anal. Calc. for $C_{26}H_{32}N_2O_{15}$ (612.5): C, 50.98, H, 5.27; N, 4.57. Found: C, 50.93; H, 5.49, N, 4.49.

2,3,4,2',3',4'-Hexa-O-*benzyl-6,6'-di*-O-*trityl-α,α-trehalose* (**21**). — A mixture of 6,6'-di-*O*-trityl-*α,α*-trehalose[4,7] (**20**, 5.08 g), benzyl bromide (4.8 mL), NaH (2.2 g), and *N,N*-dimethylformamide (120 mL), prepared at 0°, was stirred at room temperature for 2 days. After the careful addition of water, the mixture was concentrated at 65° under reduced pressure with repeated additions of water, and the remaining syrup was then partitioned between ether and water. The dried (Na_2SO_4) organic phase was concentrat-

ed to give a yellow material that was passed through a bed of silica gel with solvent *O*. Concentration of the filtrate gave amorphous **21** (7.73 g, 92%), R_F 0.65 (t.l.c., solvent *N*). By precipitation from acetone–acetic acid solution by careful addition of water, an analytical sample was obtained as a white solid that sintered and melted indistinctly above 60°. The ^{1}H-n.m.r. spectrum indicated a 5:1 ratio of phenylic to benzylic protons. ^{13}C-N.m.r. data: δ 143.4 (C-1 in CPh$_3$), 138.7, 138.1, 137.9 (C-1 in CH$_2$Ph), 128.8–126.7 (multiple peaks, Ph), 94.8 (C-1), 86.2 (*Ph*$_3$C), 81.8, 80.3, 77.9, 70.7 (C-2,3,4,5), 75.9, 75.5, 72.5 (*Ph*CH$_2$), 61.5 (C-6).

Anal. Calc. for $C_{92}H_{86}O_{11}$ (1367.6): C, 80.79; H, 6.34. Found: C, 80.68; H, 6.45.

2,3,4,2',3',4'-Hexa-O-*benzyl-α,α-trehalose* (**22**). — Compound **21** (6.90 g) was detritylated with aqueous 80% acetic acid (150 mL) during 9 h at 85°, essentially as described for the crude[8] trityl ether. Chromatography[8] of the product furnished **22** (3.475 g, 78%), $[\alpha]_D$ +104° (*c* 1.6, chloroform); lit.[8] $[\alpha]_D$ +99°. The ^{1}H-n.m.r. data agreed with those reported[8]. ^{13}C-N.m.r. data (50.29 MHz): δ 138.9, 138.4, 138.2 (C-1 in CH$_2$Ph), 128.5–127.6 (multiple peaks, Ph), 93.9 (C-1), 81.6, 79.6, 77.5, 71.5 (C-2,3,4,5), 75.6, 75.0, 73.0 (*Ph*CH$_2$), 61.4 (C-6).

2,3,4,2',3',4'-Hexa-O-*benzyl-6,6'-di*-O-*(trifluoromethyl)sulfonyl-α,α-trehalose* (**23**). — Compound **22** (1.98 g) was triflated as detailed for **14**, with appropriately adjusted proportions of reagents, to give **23**, R_F 0.65 (t.l.c., solvent *G*), which, after processing, was obtained as a pale-yellow foam (2.42 g, 94%), $[\alpha]_D$ +98° (*c* 1.2, chloroform). A sample (170 mg) was purified on a small column (3 g of silica gel) by elution with 1:6 ethyl acetate–hexane, to give colorless **23** (127 mg), m.p. 106–107° (dec.). N.m.r. data: ^{1}H (200 MHz), δ 7.3 (m, 15 H, Ph), 5.13 (d, $J_{1,2}$ 3.5 Hz, H-1), 5.06–4.50 (m, 6 H, 3 *Ph*CH$_2$), 4.18–3.95 (m, 4 H, H-3,5,6,6'), 3.55 (dd, $J_{1,2}$ 3.5, $J_{2,3}$ 9.7 Hz, H-2), 3.47 (dd, J 9.3 and 9.9 Hz, H-4); ^{13}C (50.29 MHz), δ 138.3, 137.8, 137.6 (C-1 in CH$_2$Ph), 128.6–127.7 (multiple peaks, Ph), 94.5 (C-1), 81.5, 79.3, 76.3, 68.6 (C-2,3,4,5), 75.5, 75.2, 74.2, 73.2 (*Ph*CH$_2$ and C-6).

Anal. Calc. for $C_{56}H_{56}F_6O_{15}S_2$ (1147.1): C, 58.63; H, 4.92; F, 9.94; S, 5.59. Found: C, 59.76; H, 5.25; F, 8.94; S, 5.07. The values found fit a composition $C_{55.8}H_{56.2}F_{5.4}O_{14.4}S_{1.8}$, representing a product having lost 10% of its triflyl groups; apparently, the analytical sample had deteriorated in storage and transit.

2,3,4-Tri-O-*benzyl-6-deoxy-α*-D-gluco-*heptopyranosylurononitrile* *2,3,4-tri*-O-*benzyl-6-deoxy-α*-D-gluco-*heptopyranosidurononitrile* (**24**). — Crude **23** (2.25 g) was treated with KCN as described for **15**, with appropriately adjusted proportions of reagents. Conversion of **23** (R_F 0.65) into **24** (R_F 0.25) was complete after 8 h (t.l.c., solvent *G*). The crude product, isolated as for **19**, was subjected to flash chromatography (38 g of silica gel, solvent *G*), to give pure syrupy **24** (1.21 g) and **24** (0.57 g) containing a trace impurity (t.l.c.). Pure **24** had $[\alpha]_D$ + 132° (*c* 1.5, chloroform); $\nu_{max}^{CCl_4}$ 2250 cm^{-1} (CN). N.m.r. data: ^{1}H (200 MHz), δ 7.3 (m, 15 H, 3 Ph), 5.20 (d, $J_{1,2}$ 3.5 Hz, H-1), 5.09–4.60 (m, 6 H, 3 *Ph*CH$_2$), 4.15 (qn, W 19.2 Hz, H-5), 4.04 (t, $J_{2,3} \approx J_{3,4} \approx$ 9.25 Hz, H-3), 3.64 (dd, $J_{1,2}$ 3.5, $J_{2,3}$ 9.5 Hz, H-2), 3.42 (t, $J_{3,4} \approx J_{4,5} \approx$ 9.35 Hz, H-4), 2.23 (m, 2 H, H-6,6'); ^{13}C (50.29 MHz), δ 138.7, 138.1, 138.0 (C-1 in CH$_2$Ph), 128–127.5 (multiple

peaks, Ph), 117.2 (CN), 94.0 (C-1), 81.4, 80.3, 79.6, 66.9 (C-2,3,4,5), 75.6, 75.4, 73.2 (*Ph*CH_2), 20.3 (C-6).

Anal. Calc. for $C_{56}H_{56}N_2O_9$ (901.1): C, 74.65; H, 6.26; N, 3.11. Found: C, 74.56; H, 6.48; N, 3.04.

*2,3,4,-Tri-O-benzyl-6-deoxy-α-*D-gluco*-heptopyranosyluronamide 2,3,4-tri-O-benzyl-6-deoxy-α-*D-gluco*-heptopyranosiduronamide* (**25**). — To a solution of **24** (947 mg) in acetone (30 mL) was added solid NaOH (535 mg) and aqueous 30% H_2O_2 (10 mL). The mixture was stirred at room temperature for 20 h, during which time **24** (R_f 1.0) was converted into one major product (R_f 0.7) accompanied by traces of more-polar and less-polar by-products (t.l.c., solvent *K*). No visible changes occurred on prolonged treatment of the product under these conditions or at elevated temperatures. The mixture was concentrated to a small volume, the residue was partitioned between ether and water, and the dried ($MgSO_4$) ether phase was concentrated. Column chromatography (25 g of silica gel, 99:1 ethyl acetate–methanol) of the oily residue gave **25** as a virtually pure syrup that yielded a crystalline trihydrate (825 mg, 82.5%) from ether (plus 2% of ethyl acetate) and hexane; m.p. 151–154°, $[\alpha]_D$ +77° (*c* 1, chloroform); ν_{max}^{Nujol} 3400, 3320, 3180 (NH, OH), 1680 (Amide I), 1610 (Amide II) cm^{-1}. N.m.r. data: ^1H (200 MHz), δ 7.3 (m, 15 H, 3 Ph), 5.93 and 5.73 (2 bs, 1 H each, exchangeable, NH_2), 5.18 (d, $J_{1,2}$ 3.5 Hz, H-1), 4.95–4.55 (m, 6 H, 3 *Ph*CH_2), 4.23 (m, H-5), 4.07 (t, $J_{2,3} \approx J_{3,4} \approx 10$ Hz, H-3), 3.58 (dd, $J_{1,2}$ 3.5, $J_{2,3}$ 10 Hz, H-2), 3.28 (t, $J_{3,4} \approx J_{4,5} \approx 10$ Hz, H-4), 2.55 (dd, $J_{5,6}$ 2.5, $J_{6,6'}$ 15 Hz, H-6), 2.20 (dd, $J_{5,6'}$ 10, $J_{6,6'}$ 15 Hz, H-6'); ^{13}C (50.29 MHz), δ 174.1 (CO), 138.5, 138.1, 138.1 (C-1 in CH_2Ph), 128.6–127.8 (multiple peaks, Ph), 92.3 (C-1), 81.2, 81.0, 79.4, 68.0 (C-2,3,4,5), 75.5, 74.9, 73.2 (*Ph*CH_2), 38.0 (C-6). There was an unexplained signal (secondary or quaternary C) at δ 109.6.

Anal. Calc. for $C_{56}H_{60}N_2O_{11} \cdot 3H_2O$ (991.1): C, 67.86; H, 6.71; N, 2.83. Found: C, 67.94; H, 6.60; N, 2.87.

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REFERENCES

1 H. H. Baer, M. Mekarska, and F. Bouchard, *Carbohydr. Res.*, 136 (1985) 335–345; H. H. Baer, *ACS Symp. Ser.*, 386 (1989) 22–44.

2 E. Lederer, *Pure Appl. Chem.*, 25 (1971) 135–165; A. D. Elbein, *Adv. Carbohydr. Chem. Biochem.*, 30 (1974) 227–256; M. B. Goren, in G. P. Youngmans (Ed.), *Tuberculosis*, Saunders, Philadelphia, 1979, pp. 63–193; E. Lederer, in G. P. Kubica and L. G. Wayne (Eds.), *The Mycobacteria — A Source Book*, Dekker, New York, 1984, pp. 361–378; N. Rastogi and H. L. David, *Biochimie*, 70 (1988) 1101–1120.

3 H. H. Baer and H. R. Hanna, *Carbohydr. Res.*, 102 (1982) 169–183.

4 H. Bredereck, *Ber.*, 63 (1930) 959–965.
5 C. Birch and A. C. Richardson, *Carbohydr. Res.*, 8 (1968) 411–415; R. Toubiana, M. J. Toubiana, B. C. Das, and A. C. Richardson, *Biochimie*, 55 (1973) 569–573.
6 W. E. Bachmann and W. S. Struve, *Org. React.*, 1 (1942) 38–62.
7 A. Liav and M. B. Goren, *Carbohydr. Res.*, 84 (1980) 171–174.
8 A. Liav and M. B. Goren, *Chem. Phys. Lipids*, 27 (1980) 345–352.
9 M. B. Goren and K. -J. Jiang, *Carbohydr. Res.*, 79 (1980) 225–234.