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SYNTHESIS OF 2 3,4,6-TETRA-*O*-BENZYL-L-IDOPYRANOSE

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ABSTRACT

A synthesis of 2,3,4,6-tetra-*O*-benzyl-L-idopyranose (**15**) is described based on L-sorbose as the starting material By a succession of well known, high-yielding procedures, the ketose was converted into a 2 1 mixture of 1,3,4,5-tetra-*O*-benzyl-2-*O*-(*tert*-butyldimethylsilyl)-L-iditol and -L-gulitol (**8** and **12**, respectively) Oxidation of these products to *aldehydo* forms, and removal of the *O*-silyl substituents afforded **15** and 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**17**), which were then separated Compound **17** also served as a source of **8** and **12** through reduction, and partial isomerization at C-2 to give a 1 1 mixture of 1 3,4,5-tetra-*O*-benzyl-L-iditol and -L-gulitol, followed by appropriate substitution at O-2

INTRODUCTION

The object of this study was to prepare L-idose, for use in the synthesis of L-iduronic acid-containing oligosaccharides related structurally to heparin There are two well-established routes to compounds having the L-*ido* configuration One involves[1–3] nucleophilic displacement of a 5-sulfonate of 1,2-*O*-isopropylidene-α-D-glucofuranose to produce the configurational inversion* required at C-5 In the second[7], 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose is condensed with cyanide, and the epimeric L-*ido* and D-*gluco* cyanohydrins formed are hydrolyzed to carboxylic acids, which are then separated, to furnish 1,2-*O*-isopropylidene-β-L-idofuranuronic acid To be used in the aforementioned oligosaccharide syntheses these furanose derivatives then require rearrangement into an appropriate, pyranose form[8] The present study was concerned with a different approach, one in which a readily available pyranose is converted into an L-idopyranose derivative suitable for glycosylation reactions that is, a procedure is described (see Scheme 1) whereby 2,3,4,6-tetra-*O*-benzyl-L-idopyranose (**15**) was synthesized from α-L-sorbopyranose

*For related syntheses, the configuration of C-5 of 1,2-*O*-isopropylidene-α-D-glucofuranurono-6,3-lactone[4], or of the corresponding hexodialdo derivative[5], has been similarly inverted By contrast, an attempt to promote an analogous inversion at C-5 of 2,3,4,6-tetra-*O*-benzyl-1,5-di-*O*-mesyl-D-glucitol, with potassium superoxide as the nucleophile, led to elimination[6]

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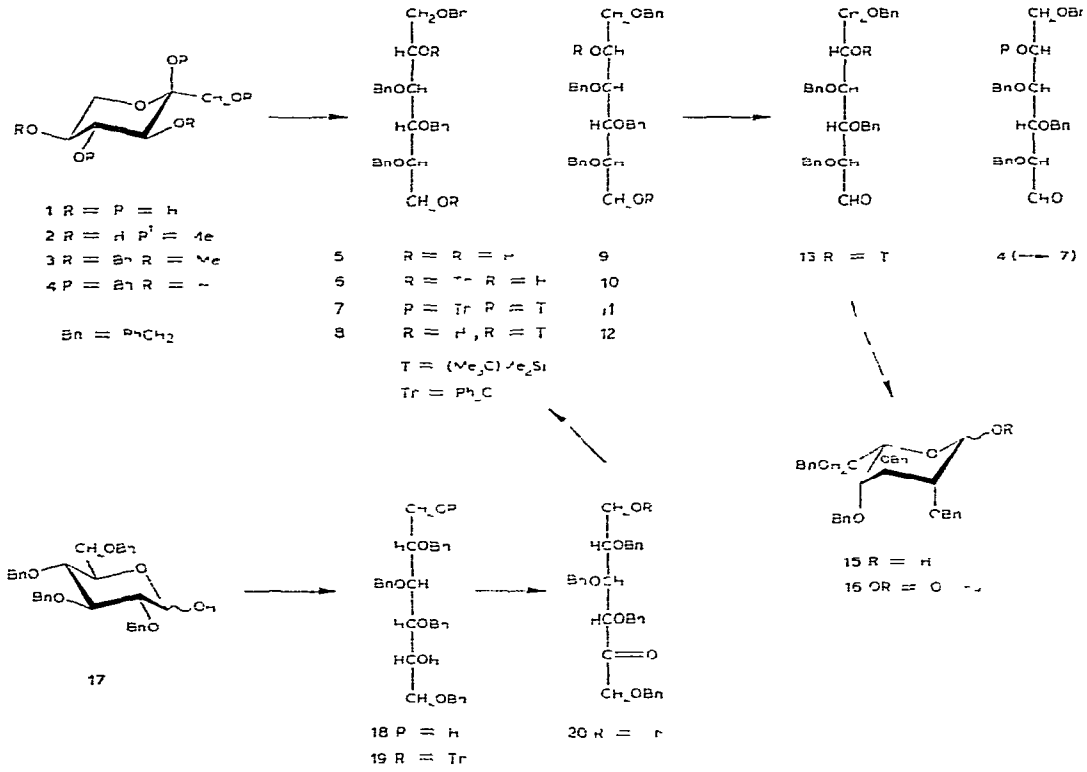

Scheme 1 Synthesis of 2,3,4,6-tetra-*O*-benzyl-L-idopyranose (**15**) starting from L-sorbose (**1**) or 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**17**)

(**1**) In a complementary synthesis of **15** (see Scheme 1), 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose* (**17**) served as the starting material

RESULTS AND DISCUSSION

Employing well-known procedures, L-sorbose (**1**) was transformed successively into methyl α-L-sorbopyranoside (**2**), methyl 1,3,4,5-tetra-*O*-benzyl-α-L-sorbopyranoside (**3**), and 1,3,4,5-tetra-*O*-benzyl-L-sorbopyranose (**4**) On reduction of **4** with sodium borohydride in methanol, a 2 1 mixture of 1,3,4,5-tetra-*O*-benzyl-L-iditol and -L-gulitol (**5** and **9**) was obtained This syrupy mixture, which was not adequately separable by chromatography, was then converted into the *O*-trityl derivatives (**6** and **10**)**

The latter mixture of **6** and **10** was also prepared by a second route 2,3,4 6-tetra-

*Available commercially as the crystalline, α anomer

In attempting to obtain crystalline intermediates, **5 and **9** were also converted into 6-(methoxy)trityl ethers, as well as the 2-*O*-acetyl and 2-*O*-benzoyl derivatives of the ethers However, all of these compounds were syrups

O-benzyl-D-glucopyranose (**17**) was reduced with sodium borohydride in 70% aqueous oxolane (tetrahydrofuran)†, and the product (**18**) was substituted at O-6 with a trityl group, giving **19**, which was oxidized to **20** with pyridine dichromate–pyridinium trifluoroacetate[9] Reduction of ketone **20** with sodium borohydride in 70% aqueous oxolane at room temperature then afforded **6** plus **10** although in this instance, the epimeric ratio§ was ~1 1 Both mixtures of **6** and **10** were used in continuing the sequence of reactions leading to **15**

A *tert*-butyldimethylsilyl group was then introduced at O-2 of **6** and **10**, yielding **7** and **11** which were separated by column chromatography on silica gel The faster-moving compound was shown to be **11**, as it was indistinguishable from the 5-*O*-(*tert*-butyldimethylsilyl) derivative prepared from **19** Accordingly, the L-*ido* epimer (**7**) was hydrolyzed briefly with aqueous acetic acid to remove the *O*-trityl substituent selectively and the alditol (**8**) produced was oxidized to an aldehyde (**13**) with pyridinium chlorochromate[10] On more-prolonged hydrolysis with aqueous acetic acid, the *O*-silyl protecting group was removed permitting cyclization and the formation of 2 3,4,6-tetra-*O*-benzyl-L-idopyranose (**15**)

The same sequence of reactions, conducted without prior separation of 7 and **11** gave a succession of the corresponding mixed, epimeric products, *i e* , **8** plus **12**, then **13** plus **14** and, finally, a mixture of 2,3,4,6-tetra-*O*-benzyl-L-idopyranose (**15**) and -D-glucopyranose (**17**) Most of product **17** was readily separated from the L-*ido* isomer as the crystalline, α anomer to afford a syrup comprised almost exclusively of **15**, that was purified further by column chromatography The L-*ido* configuration of **15** was confirmed in the following way the compound was reduced with borohydride. the *O*-benzyl groups were removed by hydrogenolysis, and the product was acetylated, giving crystalline L-iditol hexaacetate

TABLE I

PROTON COUPLING-CONSTANTS OF IDOPYRANOSE DERIVATIVES

Compound	*Spacings (Hz)*						
	1 2	*2 3*	*3 4*	*4 5*	*5 6*	*5 6*	*1 3*
1-*O*-Acetyl-2,3,4 6-tetra-*O*-benzyl-α-L-idopyranose (**16**)[a]	4 0	5 0	5 0	3 8	4 0	5 0	<0 1
1,2,3,4,6-Penta-*O*-acetyl-α-D-idopyranose[b c]	2 1	3 6	3 5	2 1	6 0	—	1 0
1,2,3,6-Tetra-*O*-acetyl-α-D-idopyranose[a c]	2 0	3 4	3 4	—	—	—	1 1

[a]Solvent, $CDCl_3$; [b]Solvent, acetone-d_6; [c]Ref 12

†When the reduction was conducted in 2-propanol, elimination of H-2 and the 3-benzyloxy group occurred, affording the corresponding enol ether in 50% yield[b]

§Estimated from the ^{1}H-n m r spectrum of the acetylated material

On acetylation of **15** with acetic anhydride–pyridine, a 3:2 mixture of the α- and β-monoacetates was formed, the α anomer (**16**) being isolated by column chromatography. In Table I, vicinal, proton–proton coupling-data for **16** are compared with those[11,12] for 1,2,3,4,6-penta- and 1,2,3,6-tetra-*O*-acetyl-α-D-idopyranose, which adopt the $^4C_1$(D) conformation almost exclusively. The larger coupling-constants for **16** showed that a mixture of conformations is present; relative to data reported[12] for various idopyranose derivatives, the ratio of the $^1C_4$(L) (**16**) to $^4C_1$(L) conformations is* ~2:1. This is comparable to the characteristics[12] of methyl 2,3,4,6-tetra-*O*-methyl-α-D-idopyranoside in the same solvent, and hence is consistent with the destabilization anticipated for 1,3-*syn*-diaxial, ether substituents, as compared with acetoxyl substituents.

EXPERIMENTAL

General methods. — Solutions were usually evaporated below 40° under diminished pressure. Optical rotations were determined at room temperature, for solutions in 1-dm tubes, with a Carl Zeiss polarimeter (Model 367732). Silica gel for column chromatography was obtained from Macherey Nagel and Co. Proton magnetic resonance spectra were recorded with Varian HA-100 and XL-200 spectrometers. ^{13}C-N.m.r. spectra were recorded at 22.6 MHz with a Bruker WH-90 spectrometer. Chemical shifts (δ) are reported with reference to tetramethylsilane.

Methyl α-L-sorbopyranoside (**2**). — Compound **1** was prepared by a procedure similar to that of Arragon and Bertrand[14]. Dry L-sorbose (80 g) was added to a solution of acetyl chloride (24 mL) in methanol (2.7 L) at 5°, with stirring. After 3 days, the solution was made neutral with silver carbonate, decolorized with charcoal (Norite), and evaporated, and the syrupy residue was exhaustively extracted with boiling acetone (2.5 L). Crystals of **2** (60 g, 70%) were obtained from the cooled extract; m.p. 119–120°. $[\alpha]_D$ −86.5° (*c* 1.0, water) (lit.[14] m.p. 118.5°, $[\alpha]_D$ −90.2°).

*Methyl 1,3,4,5-tetra-*O*-benzyl-α-L-sorbopyranoside* (**3**). — The procedure was similar to that described by Glaudemans and Fletcher[15]. Methyl α-L-sorbopyranoside (**2**; 17.5 g) and powdered potassium hydroxide (100 g) were suspended in 1,4-dioxane (100 mL). The mixture was stirred and gently boiled under reflux while benzyl chloride (125 mL) was added during 20 min. One hour later, the solvent was distilled off, water and diethyl ether were introduced with vigorous shaking, and the organic layer was separated, washed with water, and concentrated. Benzyl alcohol and dibenzyl ether were removed from the residue by distillation at 140°/20 μm Hg, affording **3** as a yellow oil (46 g, 92%), $[\alpha]_D$ −14.2° (*c* 3.1, chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 7.4–7.1 (m, 20 H, 4 C_6H_5), 5.0–4.4 (8 H, overlapping, 4 CH_2),

*The α anomer of aldose **15** probably has a similar conformational equilibrium, because H-1 (δ 5.1) exhibits the same value of $J_{1,2}$ (4.0 Hz) as does **16**. Comparable data for H-1 of the β anomers of **15** and **16** are δ 4.9 ($J_{1,2}$ 2.0 Hz) and δ 6.1 ($J_{1,2}$ 2.5 Hz), respectively; these relatively small couplings, generally characteristic[12,13] of β-idopyranose derivatives, suggest a heavy preponderance of the $^1C_4$ conformation in the β-L series.

4.1–3.3 (overlapping m, 7 H, H-1–6′), and 3.2 (s, 3 H, CH_3); ^{13}C-n.m.r. data ($CDCl_3$): 138.9, 138.6, 138.4, 137.5 (4 aryl quat. C), 129–127 (aryl C-2′–6′) 100.4 (C-1), 82.4, 79.2, 78.3, 75.4 (2), 73.3, 73.0, 68.9, 60.9 (C-6), and 48.3 p.p.m. (CH_3).

1,3,4,5-Tetra-O-*benzyl*-α-L-*sorbopyranose* (**4**). — A solution of **3** (18.5 g) in 1,4-dioxane (125 mL) was heated under reflux in the dark, and 0.5M hydrochloric acid (32 mL) was added dropwise. Heating was continued for 3 h when, according to t.l.c. (9:1 chloroform–ether), hydrolysis of **3** was complete. Ice–water (100 mL) was introduced, the mixture was extracted with chloroform, and the extract was successively washed with water, saturated sodium hydrogencarbonate, 2M hydrochloric acid, and water, dried (anhydrous sodium sulfate), and evaporated, to give **4** as an oil (15.3 g, 83%) that partially crystallized in the cold; m.p. 47–50°, $[\alpha]_D$ −11.3° (*c* 1.5, chloroform); lit.[16] m.p. 48–51°, $[\alpha]_D$ −12.9°; ^{1}H-n.m.r. data ($CDCl_3$): δ 7.4–7.0 (m, 20 H, C_6H_5), 4.9–4.4 (8 H, overlapping, 4 CH_2), and 4.1–3.3 (overlapping m, 7 H, H-1–6′).

1,3,4,5-Tetra-O-*benzyl*-L-*iditol* (**5**) *and* -L-*gulitol* (**9**). — To a stirred solution of **4** (14 g) in methanol (100 mL) at 5° was added sodium borohydride (3 g) during 0.5 h; the temperature was raised to, and kept for 3 h, at 25°, and an excess of Amberlite IR-120 (H^+) ion-exchange resin was then introduced. Borate was removed as methyl borate, affording a mixture of **5** and **9** as an amorphous residue (12.8 g, 91%); $[\alpha]_D$ +10.3° (*c* 2, chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 7.3–7.2 (m, 20 H, C_6H_5), 4.7–4.4 (8 H, overlapping, 4 CH_2), 4.1–3.3 (overlapping m, 8 H, H-1–6′), and 2.6 (m, 2 H, OH-1 and -5); ^{13}C-n.m.r. data ($CDCl_3$): 61.1 (C-6 of **5**) and 61.0 (C-6 of **9**) p.p.m.; ratio 2:1.

1,3,4,5-Tetra-O-*benzyl*-L-*gulitol* (**18**). — To a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (10 g; Pfanstiehl) in 7:3 oxolane–water (140 mL) was added sodium borohydride (10 g), and the solution was boiled under reflux for 12 h, and then evaporated. Water was introduced, the mixture was extracted with chloroform, and the extract was washed successively with 5% hydrochloric acid, saturated sodium hydrogencarbonate, and water, dried (anhydrous sodium sulfate), and evaporated, to give a viscous oil (10.3 g, ~100%); ^{1}H-n.m.r. data ($CDCl_3$): δ 6.9–6.8 (m, 20 H, C_6H_5), 4.40, 4.36, 4.30, 4.20 (s, 8 H, 4 CH_2), 4.0–3.3 (overlapping m, 8 H, H-1–6′), 2.85 (d, 1 H, OH-2, *J* 6.0 Hz), and 2.15 (t, 1 H, OH-6, *J* 6.0 Hz).

1,3,4,5-Tetra-O-*benzyl*-2-O-(tert-*butyldimethylsilyl*)-6-O-*trityl*-L-*iditol* (**7**) *and* -L-*gulitol* (**11**). — The mixture (10 g) of **5** and **9** was dissolved in pyridine (60 mL), chlorotriphenylmethane (5.5 g) was added, and, after 48 h, the solution was poured into ice–water. The opaque syrup that was deposited was dissolved in dichloromethane, and the solution was washed successively with 5% hydrochloric acid, saturated sodium hydrogencarbonate, and water, dried (anhydrous sodium sulfate), and evaporated, yielding a mixture of **6** and **10** as an oil (12.9 g, 89%). A mixture of this oil (10 g, 12.7 mmol) with *tert*-butyl-chlorodimethylsilane[17] (2.3 g, 15.2 mmol) and imidazole (2.2 g, 31.7 mmol) was dissolved in dry *N*,*N*-dimethylformamide (40 mL), and the solution was kept for 48 h at 35°, and then poured into ice–water. The product was extracted into dichloromethane, and the extract was washed suc-

cessively with 5% hydrochloric acid, saturated sodium hydrogencarbonate, and water. dried (anhydrous sodium sulfate), and evaporated The residue was purified by chromatography on a column of silica gel (700 g) with 19 1 chloroform–ether (containing a few drops of triethylamine) as the eluant, giving an oil (9 8 g 86%). $[\alpha]_D$ +5 7° (*c* 2 5, chloroform). ^{1}H-n m r data ($CDCl_3$) δ 0 82 [s 9 H, $(CH_3)_3C$]. and 0 13 and 0 05 [2 s 6 H $(CH_3)_2Si$]

1,3 4,5-Tetra-O-*benzyl-2*-O-(tert-*butyldimethylsilyl*)-L-*iditol* (**8**) *and* -L-*gulitol* (**12**) — The mixture (4 7 g) of **7** and **11** was dissolved in glacial acetic acid (9 5 mL) the solution was immediately placed on a steam bath and 70% acetic acid (38 mL preheated to ~90°) was added dropwise during 12 min oiling out of the product being avoided Ice–water was added, the precipitate that formed was dissolved in dichloromethane. and the solution was successively washed with saturated sodium hydrogencarbonate and water dried (anhydrous sodium sulfate), and evaporated to an oily residue from which most of the triphenylmethanol and some starting material were removed by distillation at 140°/20 *u*m Hg. the product was further purified by chromatography on a column of silica gel (300 g) with 24 1 benzene–ether as the eluant affording **8** and **12** as an oil (2 4 g, 65%). $[\alpha]_D$ −6 9° (*c* 1 5. chloroform), ^{1}H-n m r data ($CDCl_3$) δ 7 4–7 1 (m, 20 H, 4 C_6H_5), 4 9–4 3 (8 H, overlapping, 4 CH_2) 4 2–3 4 (overlapping m 8 H. H-1–6′) 2 35 (m 1 H, OH) 0 87 [s, 9 H. $(CH_3)_3C$], and 0 13 and 0 05 [2 s, 6 H $(CH_3)_2Si$]

2,3,4 6-Tetra-O-*benzyl-5*-O-(tert-*butyldimethylsilyl*)-L-*idose* (**13**) *and* -D-*glucose* (**14**) — Pyridinium chlorochromate (1 03 g, 4 76 mmol) and anhydrous sodium acetate (0 08 g) were suspended in dichloromethane (5 mL) and a solution of **8** and **12** (2 1 g, 3 15 mmol) in dichloromethane (10 mL) was introduced with stirring After 3 h. diethyl ether (50 mL) was added, causing deposition of a solid that was triturated, filtered off. and washed with ether The filtrate and washings were combined and evaporated, and the residue was chromatographed on a column of silica gel (100 g). with dichloromethane as the eluant affording an oil (1 54 g, 74%) $[\alpha]_D$ −2 5° (*c* 2 0, chloroform), ^{1}H-n m r data ($CDCl_3$) δ 9 68 (*ido*) and 9 60 (2 s, 2 H 2 CHO), 7 4–7 1 (m 20 H, 4 C_6H_5), 4 9–4 3 (8 H, overlapping 4 CH_2), 4 2–3 3 (overlapping m, 6 H, H-2–6′), 0 85 [s, 9 H, $(CH_3)_3C$], and 0 15 and 0 08 [2 s, 6 H. $(CH_3)_2Si$] ^{13}C-n m r data ($CDCl_3$) 198 6 (CHO), 137 6–136 4 (aryl quat C) 128 3–126 7 (aryl CH) 79.7–70 6 (18 C CH_2, C-2–6), 25 1 [$(CH_3)_3$], and −5 5 p p m [$(CH_3)_2Si$]

2 3,4 6-Tetra-O-*benzyl*-D-*glucopyranose* (**17**) — The product of oxidation (**13** + **14**) (3 3 g) was dissolved in acetic acid (30 mL), the solution was heated on a steam bath in the dark, and water (8 mL) was introduced, with stirring After 4 h at ~95°. the solution was cooled, whereupon **17** crystallized out, and was filtered off (yield. 0 8 g). the filtrate was evaporated, and the residue was dissolved in methanol, affording an additional 0 1 g of crystalline **17** (total yield 33%) m p 150–152°, $[\alpha]_D$ +20 8° (*c* 2 4, chloroform)

2,3,4,6-Tetra-O-*benzyl*-L-*idopyranose* (**15**) — Evaporation of the methanolic mother liquor from the preceding experiment gave **15** as an oil (1 7 g, 63%), $[\alpha]_D$

−1 0° (*c* 2 4, chloroform), ^{1}H-n m r data ($CDCl_3$) δ 5 15 (H-1, γ anomer) and 4 92 (H-1, β anomer) ^{13}C-n m r data ($CDCl_3$) 93 3 (C-1 β anomer) and 91 8 p p m (C-1, α anomer)

Methyl α- and β-L-idopyranosides — A solution of **15** (0 3 g) in 3% methanolic hydrogen chloride (10 mL) was boiled under reflux for 6 h, made neutral with silver carbonate, and evaporated The product was dissolved in 9 1 1,4-dioxane–water (15 mL), and *O*-debenzylated by hydrogenolysis during 18 h at 25° in the presence of palladium black (45 mg) the suspension was filtered through Celite and the filtrate was evaporated, to give an oil $[\gamma]_D$ −30 5° (*c* 1 5, chloroform), ^{1}H-n m r data (D_2O) δ 4 90 (d, H-1β, $J_{1,2}$ 1 4 Hz), 4 70 (d, H-1α, $J_{1,2}$ 4 0 Hz), and 3 55 (s, β-CH_3) 3 45 (s γ-CH_3) ratio α β = 7 3 ^{13}C-n m r data (D_2O) (γ anomer), 102 0 (C-1) 72 0 (C-3), 71 5 (C-5), 71 2 (C-2), 70 7 (C-4), 60 7 (C-6), and 56 3 (CH_3) p p m (β anomer), 100 9 (C-1), 76 0 (C-3) 70 4 (C-2), 70 1 (C-4), 69 2 (C-5) 62 0 (C-6) and 57 4 p p m (CH_3)

1,2,3,4,5,6-Hexa-O-acetyl-L-iditol — To a solution of **15** (0 25 g) in methanol (5 mL) at 5° was slowly added sodium borohydride, and the solution was then kept for 14 h at 20° An excess of Dowex-50 (H^+) ion-exchange resin was introduced, the suspension was filtered, the filtrate evaporated, and residual borate removed by repeated addition and evaporation of methanol The product was *O*-debenzylated by catalytic hydrogenolysis as already described, and the product was acetylated with acetic anhydride in the presence of anhydrous sodium acetate, affording the title compound (60 mg, 66%), m p and mixed m p 122–124° $[\gamma]_D$ +20 1° (*c* 0 3 chloroform)

1-O-Acetyl-2,3,4 6-tetra-O-benzyl-γ-L-idopyranose (**16**) — A mixture (2 0 g) of **7** and **11** was chromatographed on a column of silica gel (200 g packed in petroleum ether) by elution with petroleum ether containing a few drops of triethylamine (to prevent hydrolysis of the *O*-trityl groups by the adsorbent) and increasing proportions of chloroform Compound **11** (0 8 g) emerged first (indistinguishable by ^{1}H-n m r spectroscopy from the corresponding derivative prepared from **19**), followed by a mixture of **7** and **11**, and finally, compound **7** (0 8 g) The last was converted into **15** by the sequence described for **7** when admixed with **11** Compound **15** was acetylated with acetic anhydride, and the anomeric mixture of acetates was chromatographed on a column of silica gel (t l c grade, packed in petroleum ether) by elution with petroleum ether containing increasing proportions of chloroform affording pure α anomer **16** initially, and then mixtures of the anomers ^{1}H-n m r data for **16** ($CDCl_3$) δ 7 63–6 93 (m, 20 H, 4 C_6H_5), 6 28 (d, 1 H, H-1), 4 83 and 4 74 (2 H, AB, OCH_2, *J* 12 Hz), 4 75 and 4 60 (2 H, AB, OCH_2 *J* 12 Hz) 4 69 and 4 61 (2 H, AB, OCH_2, *J* 12 Hz), 4 64 and 4 59 (2 H, AB, OCH_2, *J* 12 Hz), 4 38 (dt, 1 H, H-5), 3 92 (dd, 1 H, H-3), 3 83 (dd, 1 H, H-6, $J_{6,6}$ 10 2 Hz), 3 81 (dd, 1 H, H-6′), 3 72 (dd, 1 H, H-4), 3 65 (dd, 1 H H-2), and 2 04 (s, 3 H, CH_3) for other ^{1}H-n m r data, see Table I

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REFERENCES

1 A S MEYER AND T REICHSTEIN, *Helv Chim Acta* 29 (1946) 152–162
2 L VARGHA, *Chem Ber* 87 (1954) 1351–1356
3 J KOVAR, *Can J Chem* 48 (1970) 2383–2385
4 R CSUK, H HONIG, J NIMPF AND H WEIDMANN, *Tetrahedron Lett*, (1980) 2135–2136
5 I MACHER K DAX, E WANEK AND H WEIDMANN, *Carbohydr Res* 80 (1980) 45–51
6 V S RAO AND A S PERLIN *Can J Chem*, in press
7 F SHAFIZADEH AND M L WOLFROM *J Am Chem Soc* 77 (1955) 2568–2569
8 J KISS AND P C WYSS, *Tetrahedron* 32 (1976) 1399–1402
9 E J COREY AND G SCHMIDT *Tetrahedron Lett* (1979) 399–402
10 E J COREY AND J W SUGGS, *Tetrahedron Lett* (1974) 2647–2650
11 N S BHACCA, D HORTON, AND H PAULSEN *J Org Chem* 33 (1968) 2484–2487
12 H PAULSEN AND M FRIEDMANN *Chem Ber*, 105 (1972) 705–712
13 A S PERLIN B CASU G R SANDERSON, AND J TSE *Carbohydr Res*, 21 (1972) 123–132
14 G ARRAGON AND G BERTRAND, *C R Acad Sci* 199 (1934) 1231–1233
15 C P J GLAUDEMANS AND H G FLETCHER, JR, *Methods Carbohydr Chem*, 6 (1972) 373–376
16 Y RABINSOHN AND H G FLETCHER, JR, *J Org Chem* 32 (1967) 3452–3457
17 E J COREY AND A VENKATESWARLU *J Am Chem Soc* 94 (1972) 6190–6191