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# A SIMPLE PREPARATION OF α- AND β-NIGEROSE OCTAACETATE AND β-NIGEROTRIOSE HENDECAACETATE BY THE ACETOLYSIS OF AN ALKALI-SOLUBLE D-GLUCAN FROM THE FRUIT BODY OF *Laetiporus sulphureus*

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ABSTRACT

Fragmentation by controlled acetolysis of an alkali-soluble D-glucan, isolated from the fruit body of *Laetiporus sulphureus*, followed by fractionation of the products on a column of silica gel, provide a simple, preparative approach to the peracetates of 3-*O*-α-D-glucopyranosyl-D-glucose (nigerose) and of *O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-D-glucose (nigerotriose). The synthesis of methyl β-, benzyl β-, phenyl α-, and phenyl β-nigeroside, and of methyl β-nigerotrioside is described.

## INTRODUCTION

Further extension of our studies[1–3] on the chemistry of oligosaccharides required the preparation of substantial quantities of the peracetates of 3-*O*-α-D-glucopyranosyl-D-glucose (nigerose, **4**) and of *O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-D-glucose (nigerotriose, **16**). The disaccharide **4** has been prepared either by partial, acid hydrolysis of such polysaccharides as nigeran[4–6], isolichenan[7], pseudonigeran[8], and an alkali-soluble D-glucan of the fruit body of *Lentinus edodes*[9], or by acetolysis of highly branched dextrans[10–14]; and it has been characterized as the crystalline β-octaacetate[6–14] **7**. In the course of these preparations of **4**, the trisaccharide **16** had been isolated in low yield on some occasions[8,9,14], and characterized as the crystalline β-hendecaacetate[8,9] **18**. In addition, **4** and **7** have been synthesized[15–21] chemically by methods based on the Koenigs–Knorr type of condensation.

Recently, it was shown that the mature fruit body of the bracket fungus *Laetiporus sulphureus* (Bull. ex Fr.) Murr. is very rich in an alkali-soluble polysaccharide composed entirely of D-glucosyl residues joined by α-D-(1→3)-glucosidic linkages[22,23]. We considered that the polysaccharide should serve as an excellent source for the preparation of a homologous series of α-D-(1→3)-linked D-gluco-oligo-

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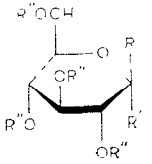
saccharides, namely, the nigerodextrins, because the fungus is widespread and grows in large clusters on live and dead trunks of hardwood species[24-27], making its collection in kilogram quantities readily possible[26,27]. We report here a simple preparation of α-nigerose octaacetate (**5**), **7**, and **18** by controlled acetolysis of an alkali-soluble D-glucan isolated from the fruit body of *L. sulphureus*. The synthesis of methyl β- (**9**), benzyl β- (**11**), phenyl β- (**13**), and phenyl α-nigeroside (**15**), and of methyl β-nigerotrioside (**20**) is also described.

## RESULTS AND DISCUSSION

An alkali-soluble D-glucan, $[\alpha]_D$ +250.5° (*c* 1.0, M sodium hydroxide), was isolated in 80% yield from the air-dried context[22,23] of the fruit body of *L. sulphureus* by a method essentially the same as that described previously[22,23]. In a trial experiment, the polysaccharide was hydrolyzed first with 90% formic acid, and then with dilute sulfuric acid, to degrees of apparent conversion into D-glucose (**1**) ranging from 40 to 55%. Paper chromatography (p.c.) of each hydrolyzate showed the presence of **1**, **4**, and **16**, in addition to higher homologs, which were all present in substantial proportions. This was not a satisfactory method for fragmentation of the polysaccharide, as our primary objective was the preparation of fairly large quantities of the di- and tri-saccharide fragments **4** and **16**.

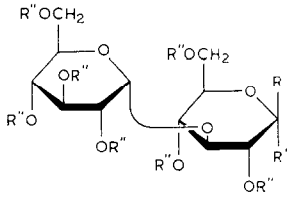



1 R, R' = H, OH, R'' = H
2 R = H, R' = OAc, R'' = Ac
3 R = OAc, R' = H, R'' = Ac

In a parallel experiment, the polysaccharide was subjected to partial fragmentation by acetolysis, using 5:5.2 (v/v) acetic anhydride–acetic acid–concentrated sulfuric acid[28]. T.l.c. examination showed that the di- and tri-saccharide fragments were now present in much greater proportion than when they were formed by hydrolysis with aqueous acid. Correspondingly, the proportions of the mono-, di-, and tri-saccharide fragments were increased, whereas those of the higher homologs were considerably diminished. Accordingly, a large amount of the polysaccharide was acetolyzed under conditions similar to those employed in the preliminary experiment, and a portion (50 g) of the acetolyzate was fractionated by chromatography on a column of silica gel.

The fastest-moving component, obtained in crystalline form (11.1 g), had physical constants identical with those of 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose[29] (**2**).

The component eluted next from the column was obtained in crystalline form (14.1 g), and proved to be **5** by its *O*-deacetylation and conversion into the known[6-14] **7**. *O*-Deacetylation of **5** with methanolic sodium methoxide gave **4**. Compound **5** was transformed into the highly crystalline 2,4,6-tri-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-glucopyranosyl bromide (**6**) with hydrogen bromide in acetic acid. Treatment of **6** with mercuric acetate in acetic acid furnished the known[6-14] **7**. The n.m.r. spectrum of **5** in chloroform-*d* showed the H-1 resonance at δ 6.33 as a doublet (*J* 3.5 Hz), consistent with the α configuration at C-1. Compound **5** was obtained in two crystalline forms; one consisted of needles having a broad m.p. of 110–114°, and the other, of prisms having m.p. 172–173°.

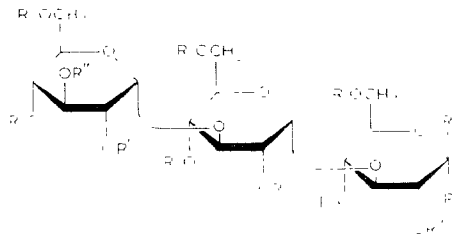



4 R, R' = H, OH, R" = H
5 R = H, R' = OAc, R" = Ac
6 R = H, R' = Br, R" = Ac
7 R = OAc, R' = H, R" = Ac
8 R = OMe, R' = H, R" = Ac
9 R = OMe, R' = R" = H
10 R = OBzl, R' = H, R" = Ac
11 R = OBzl, R' = R" = H
12 R = OPh, R' = H, R" = Ac
13 R = OPh, R' = R" = H
14 R = H, R' = OPh, R" = Ac
15 R = R" = H, R' = OPh

Bzl = $PhCH_2$

The third component eluted from the column moved as a single component in t.l.c. in a variety of solvent systems, and was obtained as an amorphous powder (8.4 g), which was shown to be a mixture of α-nigerotriose hendecaacetate (**17**) and **18**, in which **17** preponderated, on the basis of the following observations. On *O*-deacetylation, the derivative gave **16**, which showed a single spot in p.c., and was identified as the crystalline **18**, by acetylation with hot acetic anhydride and sodium acetate, suggesting that the derivative was **17**. However, the value of the optical rotation ($[\alpha]_D$ +125.7°) observed for the derivative was lower than that expected for **17**, as **5** had $[\alpha]_D$ +122.2°. The fact that the derivative was *O*-deacetylated to give **16** as the sole product precluded the possibility of contamination of **17** with other trisaccharide derivatives that might arise from anomerization[28] of the inter-sugar D-glucosidic linkages during acetolysis of the polysaccharide. An evaluation of the ratio of the α and β anomers **17** and **18** in the mixture, by making use of the relative peak-intensities of the H-1-α and -β resonances in the n.m.r. spectrum of the mixture, was not possible, because the H-1-β resonance of **18** overlapped with the signals of other ring protons.

Attempts to isolate higher members of the nigerodextrin acetates formed as minor products, by further elution of the column, were unsuccessful.



16 R', R'' = H, OH, R''' = H

17 R' = H, R'' = OAc, R''' = Ac

18 R' = OAc, R'' = H, R''' = Ac

19 R' = OMe, R'' = H, R''' = Ac

20 R' = OMe, R'' = OH, R''' = H

Subsequently, it was found that simultaneous preparation of **7** and **18** could be readily and preferentially accomplished, without prior isolation of **5** and a mixture of **17** and **18**. The polysaccharide acetolyzate (30 g) was successively treated with hydrogen bromide–acetic acid and mercuric acetate–acetic acid, and the resulting mixture was chromatographed on a column of silica gel to give 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose[29] (**3**, 6.4 g), **7** (8.1 g), and **18** (4.6 g), the yield of each product being comparable to that obtained by fractionation of the original acetolyzate.

Methanolysis of **6** in the presence of mercuric cyanide in dichloromethane gave crystalline methyl β-nigeroside heptaacetate (**8**), which, on *O*-deacetylation, afforded **9** in crystalline form. Condensation of **6** with benzyl alcohol in the presence of mercuric cyanide produced crystalline benzyl β-nigeroside heptaacetate (**10**). This was *O*-deacetylated to give crystalline **11**, which is a useful starting-material for the chemical modification of **4**. Treatment of **6** with phenol and potassium hydroxide in 50% aqueous 1,4-dioxane afforded crystalline phenyl β-nigeroside heptaacetate (**12**), which was *O*-deacetylated to give **13** in crystalline form. In the n.m.r. spectra of **9**, **11**, and **13** in deuterium oxide, each anomeric proton appeared in the region of δ 5.12–4.41 as a doublet with a magnitude of the coupling constants of 7.0–7.5 Hz, consistent with the β configuration at C-1. Fusion of **7** with phenol in the presence of zinc chloride[30] afforded crystalline phenyl α-nigeroside heptaacetate (**14**), which was *O*-deacetylated to give **15** in crystalline form. The n.m.r. spectrum of **15** in deuterium oxide exhibited the H-1 resonance at δ 5.67 as a doublet (*J* 3.0 Hz), consistent with the α configuration at C-1. Treatment of **18** with hydrogen bromide in acetic acid, followed by methanolysis as described for **6**, gave crystalline methyl β-nigerotrioside decaacetate (**19**), *O*-deacetylated to **20**, obtained in crystalline form.

## EXPERIMENTAL

*General methods.* — Unless stated otherwise, the general experimental conditions were the same as those described previously[3]. P.c. was performed on Whatman

No. 1 paper in 6:4:3 (v/v) 1-butanol–pyridine–water by the double-ascending method, with detection with aniline hydrogenphthalate. The following solvent systems (v/v) were used: (*1*) 3:2, (*2*) 1:1, and (*3*) 2:3 benzene–ethyl acetate.

*Isolation of an alkali-soluble* D-*glucan.* — Mature fruit body of *Laetiporus sulphureus* (Bull. ex Fr.) Murr. was collected in Ashiu Experimental Forest of Kyoto University, Kyoto. The air-dried context[22,23] of the fruit body was crushed and pulverized in a mortar. The resulting powder (200 g) was suspended in M sodium hydroxide (6 L), and the mixture was vigorously stirred for 2 h at room temperature. The alkaline suspension was centrifuged, and the brownish extract resulting was made neutral with acetic acid. The white, flocculent polysaccharide formed was collected by centrifugation, washed extensively with water, dehydrated by washing with methanol and then with ether, and dried *in vacuo* at 50°; yield 161 g. It had $[\alpha]_D^{26}$ +250.5° (*c* 1.0, M sodium hydroxide).

*Acetolysis of the polysaccharide.* — To a stirred suspension of finely pulverized polysaccharide (75 g) in acetic anhydride (375 mL), cooled to 0°, was added dropwise 5:2 (v/v) acetic acid–concentrated sulfuric acid (525 mL) during 1 h. The mixture was allowed to reach room temperature, and then stirred for 4 days. The dark-brown solution was poured into ice–water, and the mixture was made neutral with M sodium hydroxide, while being cooled, and extracted with chloroform (3 × 500 mL). The extracts were combined, successively washed with water, aqueous sodium hydrogencarbonate, and water, dried (sodium sulfate), and evaporated, to give a syrup (97 g). T.l.c. (solvent *2*) showed the product to be composed of three major components ($R_F$ 0.65, 0.44, and 0.35) and two minor components ($R_F$ 0.27 and 0.18).

*Fractionation of the acetolyzate.* — A portion (50 g) of the acetolyzate just described was dissolved in chloroform (100 mL), and the solution was applied to a column (9.5 × 110 cm) of silica gel that had been packed by using benzene. Elution of the column with solvent *1* gave 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose (**2**) (11.1 g); m.p. 111–112° (ethanol), $[\alpha]_D^{26}$ +101.2° (*c* 1.2, chloroform); lit.[29] m.p. 112–113° (ethanol), $[\alpha]_D^{25}$ +102.0° (chloroform).

Elution of the column with solvent *2* afforded 1,2,4,6-tetra-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-glucopyranose (**5**) as needles (14.1 g); m.p. 110–114° (ethanol), $[\alpha]_D^{25}$ +122.2° (*c* 1.7, chloroform).

*Anal.* Calc. for $C_{28}H_{38}O_{19}$: C, 49.56; H, 5.64. Found: C, 49.69; H, 5.55.

When this crystalline form of **5** was allowed to remain in its mother liquor, it was converted into a dimorphous form consisting of prisms, m.p. 172–173°.

Elution of the column with solvent *3* gave a mixture of *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→3)-1,2,4,6-tetra-*O*-acetyl-α- (**17**) and -β-D-glucopyranose (**18**) as an amorphous powder (8.4 g); $[\alpha]_D^{26}$ +125.7° (*c* 1.3, chloroform); t.l.c. (solvent *2*): $R_F$ 0.35.

Further elution of the column in order to obtain the slower-moving, minor components ($R_F$ 0.27 and 0.18 in solvent *2*) resulted in the isolation of impure materials.

*3*-O-α-D-*Glucopyranosyl*-D-*glucose* (**4**). — A solution of **5** (1.3 g) in anhydrous

methanol (20 mL) was treated with methanolic M sodium methoxide (1 mL). The solution was kept for 1 h at room temperature, made neutral with Amberlite IR-120 ($H^+$) ion-exchange resin, the suspension filtered, and the filtrate evaporated, to give **4** (0.63 g, 95%) as an amorphous powder that could not be crystallized: $[\alpha]_D^{22}$ +137.5 (*c* 1.0, water); p.c.: $R_{Glc}$ 0.81; lit.[7] $[\alpha]_D$ +138.8°; $[\alpha]_D^{23}$ +137 (*c* 0.508, water)[8]; m.p. 156°, $[\alpha]_D^{19}$ +125 → +138° (17 h; *c* 2.0, water)[13].

*2,4,6-Tri-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucopyranosyl bromide* (**6**). — To a chilled solution of **5** (5.0 g) in acetic acid (35 mL) was added a saturated (at 0°) solution of hydrogen bromide in acetic acid (35 mL). The mixture was stirred for 1 h at room temperature, and then diluted with dichloromethane. The solution was washed successively with iced water, aqueous sodium hydrogencarbonate, and water, dried (magnesium sulfate), and evaporated, to give a white, crystalline mass which, on recrystallization from dichloromethane–ether, afforded **6** (4.70 g, 91%); m.p. 210–211°, $[\alpha]_D^{25}$ +185.8° (*c* 1.1, chloroform); n.m.r. data (chloroform-*d*): δ 6.64 (d, 1 H, $J_{1,2}$ 3.8 Hz).

*Anal.* Calc. for $C_{26}H_{35}BrO_{17}$: C, 44.65; H, 5.04; Br, 11.42. Found: C, 44.54; H, 5.12; Br, 11.56.

Compound **6** (1.81 g, 92%) was also obtained from **7** (1.91 g), described later, by an analogous procedure.

*1,2,4,6-Tetra-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-β-D-glucopyranose* (**7**). — Compound **6** (0.52 g) was dissolved in acetic acid (10 mL) containing mercuric acetate (0.52 g), and the mixture was stirred for 4 h at room temperature. The solution was evaporated to dryness, and the residue was extracted with chloroform. The extract was washed with water, dried (sodium sulfate), and evaporated to a solid which was recrystallized from ethanol, to give **7** (0.46 g, 92%); m.p. 153–154°, $[\alpha]_D^{22}$ +83.2 (*c* 1.5, chloroform); lit.[7] m.p. 149°, $[\alpha]_D$ +84.9 (chloroform); m.p. 150–152°, $[\alpha]_D^{23}$ +83 (*c* 0.485, chloroform)[8]; m.p. 150°, $[\alpha]_D^{12}$ +83° (*c* 2.1, chloroform)[13].

O-α-D-*Glucopyranosyl-(1→3)-O-α-D-glucopyranosyl-(1→3)-D-glucose* (**16**). — Treatment of a mixture of **17** and **18** (6.28 g) in dry methanol (80 mL) with M sodium methoxide (2 mL), followed by processing as described for **5**, gave **16** as an amorphous powder (3.08 g, 94%); $[\alpha]_D^{17}$ +182.7° (*c* 1.1, water); p.c.: $R_{Glc}$ 0.65; lit. $[\alpha]_D^{24}$ +184° (*c* 0.3, water)[8]; $[\alpha]_D$ +164 (*c* 1.0, water)[9].

O-(*2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-α-D-glucopyranosyl)-(1→3)-1,2,4,6-tetra-O-acetyl-β-D-glucopyranose* (**18**). — Compound **16** (2.75 g) was acetylated with acetic anhydride (25 mL) and sodium acetate (2 g) under reflux for 30 min. The mixture was cooled, and poured into ice–water, and the precipitate that separated was filtered off, washed with water, and dried. Recrystallization from ethanol gave **18** (4.27 g, 81%); m.p. 188–189°, $[\alpha]_D^{22}$ +105.9 (*c* 1.1, chloroform); lit. m.p. 187–188° (aqueous ethanol), $[\alpha]_D^{23}$ +120° (*c* 0.5, chloroform)[8]; m.p. 188–189°, $[\alpha]_D$ +106° (*c* 0.5, chloroform)[9].

*Fractionation of a mixture of the β-D-acetates obtained by conversion of the original polysaccharide acetolyzate.* The acetolyzate (30 g), prepared as described

earlier, was dissolved in acetic acid (140 mL), and the solution was cooled, treated with a saturated (at 0°) solution of hydrogen bromide in acetic acid (140 mL), and stirred for 1 h at room temperature. The mixture was processed as described for the preparation of **6**, and the resulting residue was dissolved in acetic acid (200 mL) containing mercuric acetate (30 g). The mixture was stirred for 5 h at room temperature, and processed as described for the preparation of **7**, to give a syrup which was fractionated on a column (5.8 × 100 cm) of silica gel. Elution with solvent *1* gave 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**3**) (6.4 g); m.p. 132–133° (ethanol), $[\alpha]_D^{20}$ +3.8° (*c* 1.0, chloroform); lit.[29] m.p. 132°, $[\alpha]_D$ +4° (chloroform).

Elution with solvent *2* gave **7** (8.1 g); m.p. and mixed m.p. 153–154° $[\alpha]_D^{24}$ +106.2° (*c* 1.0, chloroform).

Elution with solvent *3* afforded **18** (4.6 g); m.p. and mixed m.p. 188–189° (ethanol), $[\alpha]_D^{20}$ +106.2° (*c* 1.0, chloroform).

*Methyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranoside* (**8**). — Compound **6** (2.86 g) was dissolved in a mixture of anhydrous methanol (10 mL) and dry dichloromethane (50 mL) containing mercuric cyanide (1.03 g). The mixture was stirred overnight at room temperature, and then evaporated to a syrup which was dissolved in chloroform. The solution was washed successively with water, aqueous potassium bromide, aqueous sodium hydrogencarbonate, and water, dried (sodium sulfate), and evaporated. Crystallization from 2-propanol gave **8** (2.29 g, 86%); m.p. 144–145°, $[\alpha]_D^{25}$ +61.3° (*c* 1.1, chloroform).

*Anal.* Calc. for $C_{27}H_{38}O_{18}$: C, 49.85; H, 5.89. Found: C, 49.74; H, 5.97.

*Methyl 3-*O*-α-D-glucopyranosyl-β-D-glucopyranoside* (**9**). — *O*-Deacetylation of **8** (2.01 g), as described for **5**, gave **9** (0.97 g, 88%); m.p. 212–213° (aqueous ethanol), $[\alpha]_D^{25}$ +91.0° (*c* 1.0, water); n.m.r. data (deuterium oxide): δ 5.33 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1'), 4.41 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), and 3.55 (s, 3 H, OMe).

*Anal.* Calc. for $C_{13}H_{24}O_{11}$: C, 43.82; H, 6.79. Found: C, 43.90; H, 6.86.

*Benzyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranoside* (**10**). — Compound **6** (3.01 g) was dissolved in dry benzyl alcohol (15 mL) containing mercuric cyanide (1.09 g), and the mixture was stirred for 2 h at 85°. Most of the benzyl alcohol was removed *in vacuo* at 90° by repeated co-distillation with water, and the residue was dissolved in chloroform. The solution was processed, as described for **8**, to give **10** (2.72 g, 87%); m.p. 141–142° (ethanol), $[\alpha]_D^{25}$ +37.8° (*c* 1.6, chloroform).

*Anal.* Calc. for $C_{33}H_{42}O_{18}$: C, 54.54; H, 5.83. Found: C, 54.63; H, 5.74.

*Benzyl 3-*O*-α-D-glucopyranosyl-β-D-glucopyranoside* (**11**). — *O*-Deacetylation of **10** (2.5 g), as described for **5**, gave **11** (1.36 g, 91%); m.p. 230–231° (methanol), $[\alpha]_D^{25}$ +56.6° (*c* 1.5, water); n.m.r. data (deuterium oxide): δ 7.47 (s, 5 H, Ph), 5.34 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1'), 5.00, 4.74 (AB quartet, 2 H, *J* 12.0 Hz, Ph$CH_2$O), and 4.58 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1).

*Anal.* Calc. for $C_{19}H_{28}O_{11}$: C, 52.77; H, 6.53. Found: C, 52.71; H, 6.61.

*Phenyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranoside* (**12**). — A solution of phenol (0.5 g) and potassium hydroxide

(0.3 g) in water (10 mL) was mixed with **6** (1.0 g) in 1,4-dioxane (10 mL), and the mixture was stirred for 3 h at room temperature. After evaporation of the solvents, a solution of the residue in dichloromethane was washed successively with 2M sodium hydroxide and water, dried (sodium sulfate), and evaporated to a syrup that crystallized from ethanol to give **12** (0.71 g, 70%), m.p. 85–86°, $[\alpha]_D^{15}$ +61.7° (*c* 1.1, chloroform).

*Anal.* Calc. for $C_{32}H_{40}O_{18}$: C, 53.93; H, 5.66. Found: C, 54.10; H, 5.78.

*Phenyl 3-O-α-D-glucopyranosyl-β-D-glucopyranoside* (**13**). — *O*-Deacetylation of **12** (0.49 g), as described for **5**, gave **13** (0.26 g, 90%); m.p. 199–200° (ethanol), $[\alpha]_D^{14}$ +66.7° (*c* 1.0, water); n.m.r. data (deuterium oxide): δ 7.56–6.97 (m, 5 H, Ph), 5.38 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1'), and 5.12 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1).

*Anal.* Calc. for $C_{18}H_{26}O_{11}$: C, 51.67; H, 6.26. Found: C, 51.76; H, 6.33.

*Phenyl 2,4-di-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucopyranoside* (**14**). — A mixture of **7** (2.0 g), phenol (2 g), and powdered, anhydrous zinc chloride (0.25 g) was stirred for 2 h at 100°, cooled, and diluted with dichloromethane. The solution was processed as described for the preparation of **12**, to give **14** (1.27 g, 60%); m.p. 147–148° (ethanol), $[\alpha]_D^{19}$ +165.5° (*c* 1.2, chloroform).

*Anal.* Calc. for $C_{32}H_{40}O_{18}$: C, 53.93; H, 5.66. Found: C, 54.09; H, 5.60.

*Phenyl 3-O-α-D-glucopyranosyl-α-D-glucopyranoside* (**15**). — *O*-Deacetylation of **14** (0.91 g), as described for **5**, afforded **15** (0.48 g, 91%); m.p. 208–209° (ethanol), $[\alpha]_D^{14}$ +229.4° (*c* 1.0, water); n.m.r. data (deuterium oxide): δ 7.56–7.12 (m, 5 H, Ph), 5.67 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1), and 5.43 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1').

*Anal.* Calc. for $C_{18}H_{26}O_{11}$: C, 51.67; H, 6.26. Found: C, 51.80; H, 6.21.

*Methyl O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-α-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-acetyl-β-D-glucopyranoside* (**19**). — To a cooled solution of **18** (2.0 g) in acetic acid (10 mL) was added a saturated (at 0°) solution of hydrogen bromide in acetic acid (10 mL). The mixture was stirred for 30 min at room temperature, and processed as described for the preparation of **6**. The residue was dissolved in anhydrous methanol (5 mL) and dichloromethane (25 mL) containing mercuric cyanide (0.51 g), and the mixture was processed, as described for the preparation of **8**, to give **19** (1.51 g, 78%); m.p. 183–186° (ethanol), $[\alpha]_D^{19}$ +89.4° (*c* 1.6, chloroform).

*Anal.* Calc. for $C_{39}H_{54}O_{26}$: C, 49.89; H, 5.80. Found: C, 50.14; H, 5.91.

*Methyl O-α-D-glucopyranosyl-(1→3)-O-α-D-glucopyranosyl-(1→3)-β-D-glucopyranoside* (**20**). — *O*-Deacetylation of **19** (1.22 g), as described for **5**, gave **20** (0.59 g, 88%); m.p. 214–215° (ethanol), $[\alpha]_D^{19}$ +137.6° (*c* 1.6, water); n.m.r. data (deuterium oxide): δ 5.34 (d, 2 H, $J_{1',2'}$ and $J_{1'',2''}$ 3.5 Hz, H-1' and -1''), 4.38 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), and 3.56 (s, 3 H, OMe).

*Anal.* Calc. for $C_{19}H_{34}O_{16}$: C, 44.02; H, 6.61. Found: C, 44.13; H, 6.76.

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