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# Synthesis of nigero-oligosaccharides

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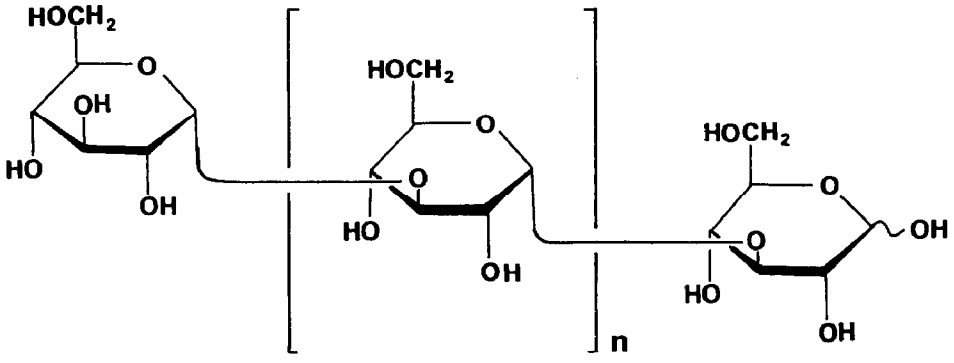
ABSTRACT

Nigerose [α-D-Glc*p*-(1→3)-D-Glc*p*], nigerotriose, nigerotetraose, and nigeropentaose have been synthesized by chain elongation starting at the reducing end, from the corresponding octa-, undeca-, tetradeca-, and heptadeca-β-D-acetates, respectively, via thioglycoside-mediated 1,2-*cis* coupling, using 1,2,4,6-tetra-*O*-acetyl-β-D-glucopyranose as the glucosyl acceptor and methyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside, methyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside, and methyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside as the donors.

## INTRODUCTION

Despite the widespread occurrence of the disaccharide fragment having the structure *O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (nigerose, **1**) in various oligo-




**1** *n* = 0

**2** *n* = 1

**3** *n* = 2

**4** *n* = 3

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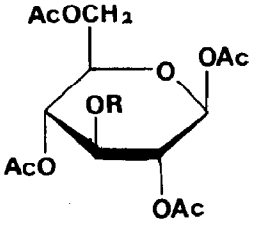
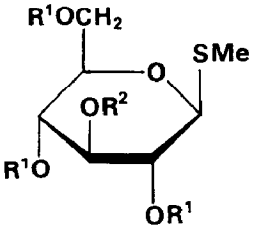
and poly-saccharides[1], disaccharide **1** does not occur free in Nature to any extent[2]. The isolation of **1** and *O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (nigerotriose, **2**) from natural sources[2,3] and the chemical synthesis of **1** have been reviewed[2-4]. Since we reported a simple preparation of **1** and **2** by acetolysis of an alkali-soluble D-glucan from the fruit body of *Laetiporus sulphureus*[3], there has been a growing demand among bio- and immuno-chemists for supplies of **1** and **2**. This led us to re-investigate a facile synthesis of **1**.

We now report an improved preparation of **1** as well as the first chemical synthesis of higher oligosaccharide homologs having (1→3)-α-D-glucosidic linkages, namely, **2**, *O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (nigerotetraose, **3**), and *O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (nigeropentaose, **4**). The tetra- (**3**) and penta-saccharide **4** have been prepared by partial acid hydrolysis of a polysaccharide from the cell wall of *Aspergillus niger*[5].

## RESULTS AND DISCUSSION

1,2,4,6-Tetra-*O*-acetyl-β-D-glucopyranose[6,7] (**8**) was chosen as the glucosyl acceptor for the preparation of **1** and **2** and prepared in 70% net yield from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**5**) according to an earlier, analogous route[6,7] with the following modifications: benzylation of **5** with benzyl bromide–sodium hydride in *N,N*-dimethylformamide[8], followed by hydrolysis of the isopropylidene groups with a cation-exchange resin[9,10] [→3-*O*-benzyl-D-glucopyranose (**6**, 91%)] and acetylation in a boiling acetic anhydride–pyridine afforded 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-β-D-




**7** R = Bzl

**8** R = H

**9** R = All

**10** $R^1 = R^2 = Bzl$

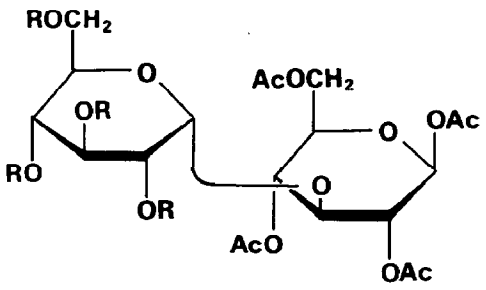
**11** $R^1 = Ac$, $R^2 = All$

**12** $R^1 = H$, $R^2 = All$

**13** $R^1 = Bzl$, $R^2 = All$

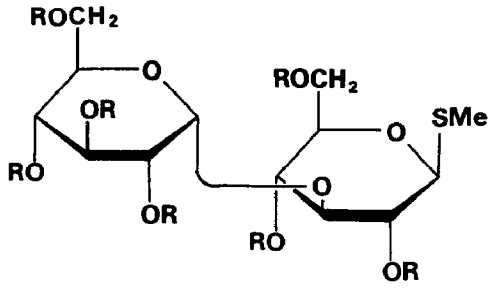
**14** $R^1 = Bzl$, $R^2 = H$

**15** $R^1 = Bzl$, $R^2 = COCH_2Cl$



**17** R = Bzl

**18** R = Ac



**19** R = Ac

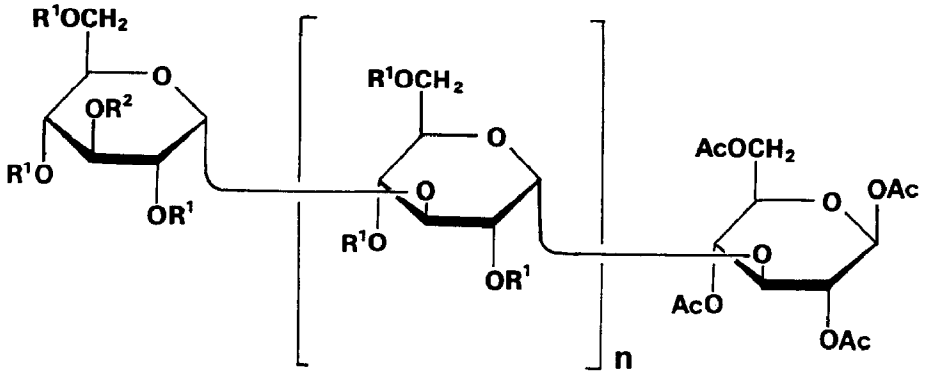
**20** R = H

**21** R = Bzl

glucopyranose (**7**, 80%). Hydrogenolysis (Pd–C) of **7** gave **8** (96%). The previous methods gave **8** in 14–56% overall yields[6,7].

Glucosidation of **8** with methyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[11] (**10**) in 1,2-dichloroethane–*N*,*N*-dimethylformamide in the presence of cupric bromide and tetrabutylammonium bromide[12] gave 77% of the crystalline α-(1→3)-linked disaccharide derivative **17** after column chromatography. In the $^{13}$C-n.m.r. spectrum of **17**, the signal for C-1′ appeared at 99.5 p.p.m., indicating[13] the α configuration at C-1′. Condensation of **8** (not sufficiently soluble in ether) with **10** in ether–1,2-dimethoxyethane in the presence of methyl triflate[14] gave 60% of **17**. Coupling of **8** with **10** in dichloromethane in the presence of methylsulfenyl bromide[15] afforded 41% of **17**. Reaction of **8** with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride[16] (**16**) in ether–1,2-dimethoxyethane in the presence of silver perchlorate and 2,4,6-trimethylpyridine[17] afforded 61% of **17**. Hydrogenolysis of **17**, followed by acetylation, afforded β-nigerose octaacetate[3] (**18**, 94%), which was *O*-deacetylated to provide compound[3] **1** (98%). Thus, the sequence **8** + **10** → **17** →**18** → **1**, using cupric bromide–tetrabutylammonium bromide as the thiophilic activator for **10** and giving **1** in 71% overall yield (based on **8**) appears to be practical for the preparation of substantial amounts of **1** and is clearly superior to the existing synthetic methods, which employed unstable glucosyl donors[17–21].

Treatment of **18** with methyl tributyltin sulfide in 1,2-dichloroethane in the presence of stannic chloride[22] gave methyl 1-thio-β-nigeroside heptaacetate (**19**, 86%). *O*-Deacetylation of **19** (→**20**) and benzylation[8] afforded the hepta-*O*-benzyl derivative **21**. Glycosylation of **8** with **21**, promoted by cupric bromide–tetrabutylammonium bromide as before gave the trisaccharide derivative **22** (63%) after column chromatography. The α configuration at the newly formed interglucosidic linkage in **22** was clear[13] from the $^{13}$C-n.m.r. signal at 96.65 p.p.m. Coupling of **8** with **21** in ether, assisted by methyl triflate as before, afforded **22** (56%). Hydrogenolysis of **22**, followed by acetylation, produced β-nigerotriose undecaacetate[3] (**23**), which was *O*-deacetylated to provide compound[3] **2**.




**22** $n$ = 1, $R^1 = R^2$ = Bzl

**23** $n$ = 1, $R^1 = R^2$ = Ac

**24** $n$ = 0, $R^1$ = Bzl, $R^2$ = All

**25** $n$ = 0, $R^1$ = Bzl, $R^2$ = H

**26** $n$ = 2, $R^1 = R^2$ = Bzl

**27** $n$ = 2, $R^1 = R^2$ = Ac

**28** $n$ = 1, $R^1$ = Bzl, $R^2$ = All

**29** $n$ = 1, $R^1$ = Bzl, $R^2$ = H

**30** $n$ = 3, $R^1 = R^2$ = Bzl

**31** $n$ = 3, $R^1 = R^2$ = Ac

Methyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**13**) and methyl 2,4,6-tri-*O*-benzyl-3-*O*-chloroacetyl-1-thio-β-D-glucopyranoside (**15**), each having a blocking group at O-3 that is selectively removable, namely, the site of further chain-extension, were prepared for the stepwise construction of the higher nigero-oligosaccharides **3** and **4**. Reaction of 1,2,4,6-tetra-*O*-acetyl-3-*O*-allyl-β-D-glucopyranose[10] (**9**) with methyl tributyltin sulfide as before gave methyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-1-thio-β-D-glucopyranoside (**11**, 82%). *O*-Deacetylation of **11** (→**12**) and then benzylation afforded **13**. Isomerization of the allyl group in **13** to the propenyl ether with potassium *tert*-butoxide[23] in *N*,*N*-dimethylformamide, followed by hydrolysis with dilute acid[23] (→**14**), and treatment with chloroacetyl chloride–pyridine in dichloromethane[24] yielded **15**.

Methyl triflate-catalyzed condensation of **8** with **13** as before gave, after column chromatography, the disaccharide derivative **24** (61%), the $^{13}$C-n.m.r. spectrum of which showed the signal for C-1′ at 99.6 p.p.m. Attempted glucosylation of **8** with **13**, promoted by cupric bromide–tetrabutylammonium bromide as before, resulted in extensive conversion of **13** into by-products having mobilities in t.l.c. lower than **13**, giving 48% of **24**. Attempts to condense **8** with **15** in the presence of methyl triflate or to couple **8** with **15** in the presence of cupric bromide–tetrabutylammonium bromide were unsuccessful; in the former reaction, a complex mixture of products was obtained (t.l.c.) and in the latter, no reaction took place between **8** and **15**, even after one week. *O*-Deallylation of **24** with palladium chloride–sodium acetate in aqueous acetic acid[25] provided the disaccharide derivative **25** having HO-3′ unsubstituted.

Glycosylation of **25** with **21** in the presence of cupric bromide–tetrabutylammonium bromide as before gave, after column chromatography, the tetrasaccharide derivative **26** (64%), the $^{13}$C-n.m.r. spectrum of which showed the signal for C-1″ at 95.5 p.p.m. Hydrogenolysis of **26**, followed by acetylation, afforded β-nigerotetraose tetradecaacetate (**27**), which was *O*-deacetylated to furnish compound[5] **3**.

Methyl triflate-promoted reaction of **25** with **13** as before gave, after column chromatography, the trisaccharide derivative **28** (59%), the $^{13}$C-n.m.r. spectrum of which displayed the signal for C-1″ at 98.7 p.p.m. *O*-Deallylation[25] of **28** afforded the trisaccharide derivative **29** having HO-3″ unsubstituted, which was coupled with **21** in the presence of cupric bromide–tetrabutylammonium bromide as before to give, after column chromatography, the pentasaccharide derivative **30** (59%), the $^{13}$C-n.m.r. spectrum of which showed the signal for C-1‴ at 95.9 p.p.m. On successive hydrogenolysis and acetylation, compound **30** provided β-nigeropentaose heptadecaacetate (**31**), which was *O*-deacetylated to furnish compound[5] **4**.

The di- (**1**), tri- (**2**), and tetra- (**3**), and penta-saccharide (**4**) were homogeneous by l.c. and gave $^{13}$C-N.m.r. spectra, consistent with the structures assigned.

## EXPERIMENTAL

*General methods.* — Unless stated otherwise, these were as described[16]. $^{13}$C-N.m.r. spectra were recorded at 22.6 MHz with a Hitachi R-90H spectrometer for solutions in $CDCl_3$ and $CD_3OD$ (internal $Me_4Si$) or $D_2O$ (internal sodium 4,4-dimethyl-4-silapentanoate-$d_4$). H.p.l.c. was performed with a Jasco 880-PU instrument equipped with a Shodex SE-61 r.i. detector and a column of YMC-pack polyamine (250 × 4.6 mm i.d., YMC, Kyoto) using 65:35 (v/v) $CH_3CN$–$H_2O$ as eluent. The following solvent systems (v/v) were used: benzene–EtOAc (*1*, 30:1; *2*, 15:1; *3*, 10:1; *4*, 6:1; *5*, 4:1; *6*, 1:1) and hexane–EtOAc (*7*, 9:1; *8*, 4:1; *9*, 2:1; *10*, 1:1).

*1,2,4,6-Tetra-O-acetyl-β-D-glucopyranose* (**8**). — Sodium hydride (10 g; 60% in mineral oil) was added portionwise at 0° to a stirred mixture of **5** (50 g, 0.19 mol) in *N*,*N*-dimethylformamide (500 mL), and the mixture was stirred for 1 h at room temperature and then cooled to 0°. Benzyl bromide (27 mL, 0.23 mol) was added dropwise and the mixture was stirred for 3 h at room temperature. Methanol was then added to decompose the excess of hydride, the solvents were evaporated, and a solution of the residue in $CH_2Cl_2$ was washed with $H_2O$ to neutrality and evaporated. A suspension of the residue and Amberlite IR-120 ($H^+$) ion-exchange resin (70 g) in water (600 mL) was stirred for 5 h at 80°. The resin was filtered off and washed successively with $H_2O$ and PhMe. The combined filtrate and washings were partitioned and the aqueous layer was made neutral (as determined with indicator paper) with solid $Li_2CO_3$. The mixture was filtered through a Celite layer and the filtrate was concentrated to dryness with the aid of repeated evaporation with EtOH. The residue was crystallized from EtOAc to give 3-*O*-benzyl-D-glucopyranose (**6**) (47.2 g, 91%), m.p. 133–134°; lit.[7] m.p. 131–133°.

To a solution of **6** (30.5 g) in pyridine (150 mL) was added $Ac_2O$ (100 mL), and the mixture was boiled under reflux for 20 min, and then cooled and evaporated. The last

traces of solvents were removed by repeated evaporation of PhMe from the residue, crystallization of which from EtOH then gave 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranose (**7**, 39.6 g, 80%), m.p. 107–108°, $[\alpha]_D^{20}$ −1° (*c* 1.2, $CHCl_3$); lit.[6] m.p. 107°, $[\alpha]_D$ −1.23° ($CHCl_3$).

A solution of **7** (30 g) in AcOH (210 mL) was hydrogenated in the presence of 10% Pd–C (5 g) at normal pressure overnight at room temperature. The suspension was filtered through a Celite pad and washed with MeOH, and the combined filtrate and washings were evaporated. Crystallization of the residue from $CH_2Cl_2$–hexane gave **8** (22.8 g, 96%), m.p. 126–127°, $[\alpha]_D^{22}$ −14° (*c* 1.3, $CHCl_3$); lit.[6] m.p. 127°, $[\alpha]_D^{20}$ −13.5° ($CHCl_3$).

O-(*2,3,4,6-Tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→3*)-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**17**). — (*a*) A mixture of $CuBr_2$ (7.50 g, 33.6 mmol), $Bu_4NBr$ (2.17 g, 6.7 mmol), and powdered 4A molecular sieve (20 g) in 1,2-dichloroethane (60 mL) and *N*,*N*-dimethylformamide (19 mL) was stirred under argon for 1 h at room temperature. A solution of **8** (6.0 g, 17.2 mmol) and **10** (12.78 g, 22.4 mmol) in 1,2-dichloroethane (30 mL) was added and the mixture was stirred for 3 days at room temperature, diluted with $CHCl_3$ (150 mL), and then filtered through a Celite pad. The solids were washed with $CHCl_3$ and the combined filtrate and washings were washed successively with aq. $NaHCO_3$ and $H_2O$, dried, and evaporated. Column chromatography (solvent *2*) of the residue gave **17** (11.55 g, 77%), m.p. 122–123° (from ether–petroleum ether), $[\alpha]_D^{25}$ +31° (*c* 1.5, $CHCl_3$); $R_F$ 0.43 (t.l.c. in solvent *4*); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.3, 169.6 (2 C), and 169.0 (C=O), 138.7, 138.3, 138.0, and 137.8 (aromatic C-1), 99.5 (C-1'), 91.8 (C-1), and 20.8, 20.7, and 20.6 (2 C) ($CO\underline{C}H_3$).

*Anal.* Calc. for $C_{48}H_{54}O_{15}$: C, 66.20; H, 6.25. Found: C, 66.14; H, 6.20.

(*b*) A mixture of **8** (0.85 g, 2.4 mmol), **10** (1.81 g, 3.2 mmol), and powdered 4A molecular sieve (10 g) in ether (30 mL) and 1,2-dimethoxyethane (3 mL) was stirred under argon for 1 h at room temperature and then cooled to 0°. Methyl triflate (1.79 mL, 15.8 mmol) was injected through a rubber septum and the mixture was stirred for 4 h at room temperature. Triethylamine (4 mL) was added and the mixture was stirred for 20 min, filtered through a Celite pad which was washed with PhMe. The combined filtrate and washings were evaporated and the residue was purified as described in (*a*) to give **17** (1.28 g, 60%).

(*c*) A mixture of **8** (0.31 g, 890 μmol), **10** (0.66 g, 1.2 mmol), and powdered 4A molecular sieve (4 g) in $CH_2Cl_2$ (15 mL) was treated a solution of M methylsulfenyl bromide in $CH_2Cl_2$ (10 mL). The mixture was stirred overnight at room temperature and then processed as described[15]. The residue was subjected to column chromatography as in (*a*), to afford **17** (0.32 g, 41%).

(*d*) A solution of **16** (1.93 g, 3.5 mmol) in ether (20 mL) was added dropwise at 0° to a stirred mixture of **8** (1.0 g, 2.9 mmol), $AgClO_4$ (0.79 g, 3.8 mmol), and 2,4,6-trimethylpyridine (0.5 mL, 3.8 mmol) in ether (50 mL) and 1,2-dimethoxyethane (2 mL) with exclusion of moisture and light. The mixture was allowed to attain room temperature and stirred for 3 h at room temperature. Insoluble material was collected on a layer of Celite and washed with PhMe, and the combined filtrate and washings were

washed successively with cold dil. HCl, aq. $NaHCO_3$, and $H_2O$, dried, and evaporated. The residue was subjected to column chromatography as described in (*a*), to give **17** (1.53 g, 61%).

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→3*)-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**18**). — The product obtained by hydrogenolysis of **17** (8.77 g) in 2-$MeO(CH_2)_2OH$ (110 mL) in the presence of 10% Pd–C (3 g), as described for the preparation of **8**, was treated with $Ac_2O$–pyridine (1:2, 60 mL) for 1 h at 70°. Processing of the mixture as described for the preparation of **7**, followed by column chromatography (solvent *6*), gave **18** (6.42 g, 94%), m.p. 152–153° (from EtOH), $[\alpha]_D^{25}$ +84° (*c* 1.2, $CHCl_3$); lit.[3] m.p. 153–154°, $[\alpha]_D$ +83.2° ($CHCl_3$).

O-α-D-*Glucopyranosyl*-(*1→3*)-D-*glucopyranose* (**1**). — A solution of **18** (0.56 g) in dry MeOH (10 mL) was treated with a catalytic amount of methanolic NaOMe. The mixture was kept for 1 h at room temperature, made neutral with Amberlite IR-120 ($H^+$) resin, diluted with $H_2O$, filtered, and evaporated to afford **1** (0.275 g, 98%), $[\alpha]_D^{25}$ +138° (*c* 1.2, $H_2O$); lit.[3] $[\alpha]_D$ +137.5° ($H_2O$); $R_{Glc}$ 1.31 (l.c.); $^{13}$C-n.m.r. ($D_2O$): δ 101.6 (C-1′), 98.5 (C-1β), 94.8 (C-1α), 84.9 and 82.4 (C-3), 78.1, 75.5, 74.3, 73.7, 72.5, 71.95, and 63.05(C-6,6′).

*Methyl* O-(*2,3,4,6-tetra-O-acetyl*-α-D-*glucopyranosyl*)-(*1→3*)-*2,4,6-tri*-O-*acetyl-1-thio*-β-D-*glucopyranoside* (**19**). —A solution of $SnCl_4$ (0.90 mL, 7.7 mmol) in 1,2-dichloroethane (10 mL) was added dropwise at 0° to a stirred solution of **18** (5.0 g, 7.4 mmol) and $Bu_3SnSMe$ (2.61 g, 7.7 mmol) in 1,2-dichloroethane (70 mL). The mixture was stirred for 2 h at room temperature, poured into ice–aq. $NaHCO_3$–aq. KF, and filtered through a Celite layer which was washed with $CH_2Cl_2$. The combined filtrate and washings were partitioned and the organic layer was washed with $H_2O$, dried, and evaporated. Column chromatography (solvent *5*) of the residue gave **19** (4.22 g, 86%), m.p. 87–88° (from ether–petroleum ether), $[\alpha]_D^{25}$ +55° (*c* 1.3, $CHCl_3$); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.4, 170.25, 169.2, and 169.1 (C=O), 96.25 (C-1′), 82.7 (C-1), 62.0 (C-6), 61.2 (C-6′), 20.8, 20.7, 20.5 ($COCH_3$), and 11.0 (SMe).

*Anal.* Calc. for $C_{27}H_{28}O_{17}S$: C, 48.65; H, 5.75. Found: C, 48.77: H, 5.80.

*Methyl* O-α-D-*glucopyranosyl*-(*1→3*)-*1-thio*-β-D-*glucopyranoside* (**20**). — A solution of **19** (4.04 g) in MeOH (50 mL) containing methanolic NaOMe (3 mL) was boiled under reflux for 40 min. The mixture was processed as described for the preparation of **1** to afford **20** (2.14 g, 95%), m.p. 214–216° (from EtOH), $[\alpha]_D^{25}$ +80° (*c* 1.1, $H_2O$); $^{13}$C-n.m.r. ($D_2O$): δ 101.8 (C-1′), 88.1 (C-1), 86.4 (C-3), 63.3 (C-6′), 62.9 (C-6), and 14.05 (SMe).

*Anal.* Calc. for $C_{13}H_{24}O_{10}S$: C, 41.93; H, 6.50. Found: C, 42.05; H, 6.56.

*Methyl* O-(*2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→3*)-*2,4,6-tri*-O-*benzyl-1-thio*-β-D-*glucopyranoside* (**21**). — A solution of **20** (2.0 g) in *N,N*-dimethylformamide (40 mL) was stirred with NaH (2.3 g; 60% in mineral oil) for 1 h at room temperature and then cooled to 0°. Benzyl bromide (6.2 mL) was added dropwise, and the mixture was stirred overnight at room temperature and process as described for the preparation of **6**. Column chromatography (solvent *8*) of the product gave **21** (4.96 g, 92%), $[\alpha]_D^{23}$ +43.5° (*c* 1.6, $CHCl_3$); $^{13}$C-n.m.r. ($CDCl_3$): δ 138.6, 138.5, 138.05 (2 C), 137.9, 137.8, and 137.4 (aromatic C-1), 97.1 (C-1′), 85.2 (C-1), and 12.6 (SMe).

*Anal.* Calc. for $C_{62}H_{66}O_{10}S$: C, 74.23; H, 6.63. Found: C, 74.35; H, 6.77.

O-(*2,3,4,6-Tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→3*)-O-(*2,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→3*)-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**22**). — (*a*) To a stirred mixture of $CuBr_2$ (0.82 g, 3.7 mmol), $Bu_4NBr$ (0.59 g, 1.6 mmol), and powdered 4A molecular sieve (4 g) in 1,2-dichloroethane (15 mL) and *N*,*N*-dimethylformamide (4 mL) was added a solution of **8** (0.69 g, 2 mmol) and **21** (2.48 g, 2.5 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred for 4 days at room temperature and processed as described for the preparation of **17**. Column chromatography (solvent *3*) of the product gave **22** (1.62 g, 63%), $[\alpha]_D^{25}$ + 55° (*c* 1.3, $CHCl_3$); $R_F$ 0.40 (t.l.c. in solvent *4*); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.4, 169.0 (2 C), and 168.9 (C = O), 138.7, 138.5, 138.3, 138.1, 138.0, and 137.8 (2 C) (aromatic C-1), 98.8 (C-1″), 96.56 (C-1′), 91.9 (C-1), and 20.8 (2 C), 20.7, and 20.4 ($COCH_3$).

*Anal.* Calc. for $C_{75}H_{82}O_{20}$: C, 69.11; H, 6.34. Found: C, 69.34; H, 6.46.

(*b*) Methyl triflate (0.51 mL, 4.5 mmol) was added at 0° to a stirred mixture of **8** (0.25 g, 717 μmol), **21** (0.90 g, 897 μmol), and powdered 4A molecular sieve (5 g) in ether (15 mL) and 1,2-dimethoxyethane (1 mL). The mixture was stirred for 5 h at room temperature and processed as described for the preparation of **17**. Column chromatography of the product as in (*a*) gave **22** (0.53 g, 56%).

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* (**23**). — Hydrogenolysis of **22** (1.75 g), followed by acetylation and purification of the product by column chromatography as described for the preparation of **18**, gave **23** (1.19 g, 92%), m.p. 188–189° (from EtOH), $[\alpha]_D^{25}$ + 107° (*c* 1.0, $CHCl_3$); lit.[3] m.p. 187–188°, $[\alpha]_D$ + 105.9°; $^{13}$C-n.m.r. ($CDCl_3$): δ 95.7 (C-1″), 95.4 (C-1′), and 91.7 (C-1).

O-α-D-*Glucopyranosyl*-(*1→3*)-O-α-D-*glucopyranosyl*-(*1→3*)-D-*glucopyranose* (**2**). — *O*-Deacetylation of **23** (0.98 g), as described for the preparation of **1**, afforded **2** (0.49 g, 96%), $[\alpha]_D^{25}$ + 182° (*c* 1.2, $H_2O$); lit.[3] $[\alpha]_D$ + 182.7° ($H_2O$); $R_{Glc}$ 1.73 (l.c.); $^{13}$C-n.m.r. ($D_2O$): δ 101.8 (2 C, C-1′, 1″), 98.6 (C-1′β), 94.85 (C-1α), 85.0 and 82.5 (C-3), 82.7 (C-3′), 78.2, 75.5, 74.4, 74.2, 73.8, 72.9, 72.7, 72.6, 72.4, 72.2, and 63.2 and 62.8 (C-6,6′,6″).

*Methyl 2,4,6-tri*-O-*acetyl-3*-O-*allyl-1-thio*-β-D-*glucopyranoside* (**11**). — A mixture of **9** (10 g, 26 mmol) and $Bu_3SnSMe$ (9.11 g, 27 mmol) in 1,2-dichloroethane (100 mL) was treated at 0° with a solution of $SnCl_4$ (3.16 mL, 27 mmol) in 1,2-dichloroethane (20 mL). Processing of the mixture as described for the preparation of **19**, followed by column chromatography (solvent *9*) of the product, gave **11** (7.94 g, 82%), $[\alpha]_D^{25}$ − 11° (*c* 1.2, $CHCl_3$); $R_F$ 0.5 (t.l.c. in solvent *10*); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.4 and 169.0 (2 C) (C = O), 134.15 and 116.7 ($CH=CH_2$), 82.9 (C-1), 20.8 (2 C) and 20.1 ($COCH_3$), and 11.15 (SMe).

*Anal.* Calc. for $C_{16}H_{24}O_8S$: C, 51.05; H, 6.43. Found: C, 51.11; H, 6.40.

*Methyl 3*-O-*allyl-1-thio*-β-D-*glucopyranoside* (**12**). — A solution of **11** (9.7 g) in MeOH (100 mL) containing methanolic M NaOMe (3 mL) was boiled under reflux for 1.5 h and processed as described for the preparation of **1**, to give **12** (6.45 g, 96%), m.p. 84–85° (from MeOH–ether), $[\alpha]_D^{25}$ − 33° (*c* 1.3, MeOH); $^{13}$C-n.m.r. ($CD_3OD$): δ 136.65 and 116.6 ($CH=CH_2$), 87.8 (C-1), 87.0 (C-3), 62.65 (C-6), and 12.0 (SMe).

*Anal.* Calc. for $C_{10}H_{18}O_5S$: C, 47.98; H, 7.25. Found: C, 47.88; H, 7.22.

*Methyl 3-O-allyl-2,4,6-tri-O-benzyl-1-thio-β-D-glucopyranoside* (**13**). — A solution of **12** (6.16 g) in *N,N*-dimethylformamide (90 mL) was treated with NaH (3.84 g; 60% in mineral oil), followed by benzyl bromide (10.4 mL). The mixture was stirred for 2 h and processed as described for the preparation of **6**. Column chromatography (solvent *7*) of the residue gave **13** (11.14 g, 94%), m.p. 89–90° (from EtOH), $[\alpha]_D^{25}$ +8° (*c* 1.5, $CHCl_3$); $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 138.1, 138.0, and 137.9 (aromatic C-1), 134.9 and 116.4 ($CH=CH_2$), 86.1 (C-1), and 12.8 (SMe).

*Anal.* Calc. for $C_{31}H_{36}O_5S$: C, 71.51; H, 6.97. Found: C, 71.55; H, 7.10.

*Methyl 2,4,6-tri-O-benzyl-1-thio-β-D-glucopyranoside* (**14**). — A solution of **13** (3.5 g) in *N,N*-dimethylformamide (30 mL) was treated with KOBu$^t$ (2 g) for 40 min at 80°. The mixture was cooled, diluted with $H_2O$, and extracted three times with $CHCl_3$. The combined extracts were washed with $H_2O$ and evaporated. A solution of the residue in $Me_2CO$–0.1M HCl (9:1, 20 mL) was boiled under reflux for 30 min, then cooled, made neutral with solid $NaHCO_3$, concentrated, and the residue was extracted with $CHCl_3$. The extract was washed with $H_2O$, dried, and evaporated. Column chromatography (solvent *9*) of the residue gave **14** (2.55 g, 79%), m.p. 32.5–34° (from pentane), $[\alpha]_D^{20}$ +7° (*c* 1.5, $CHCl_3$); $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 138.1, 138.0, and 137.9 (aromatic C-1), 84.85 (C-1), 69.0, and 12.8 (SMe).

*Anal.* Calc. for $C_{28}H_{32}O_5S$: C, 69.97; H, 6.71. Found: C, 70.11; H, 6.64.

*Methyl 2,4,6-tri-O-benzyl-3-O-chloroacetyl-1-thio-β-D-glucopyranoside* (**15**). — A solution of **14** (2.13 g) in $CH_2Cl_2$ (20 mL) containing pyridine (0.72 mL) was cooled to 0°, treated with a solution of $ClCH_2COCl$ (0.46 mL) in $CH_2Cl_2$ (5 mL), and kept for 20 min at 0°. The mixture was diluted with $CH_2Cl_2$, poured into ice–$H_2O$, and the organic layer was separated, washed successively with dil. HCl, aq. $NaHCO_3$, and $H_2O$, dried, and evaporated. Column chromatography (solvent *1*) of the residue gave **15** (2.30 g, 93%), m.p. 75–76° (from ether–hexane), $[\alpha]_D^{20}$ −2° (*c* 1.4, $CHCl_3$); $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 166.0 (C=O), 137.8, 137.6, and 137.5 (aromatic C-1), 40.5 ($COCH_2Cl$), 85.3 (C-1), and SMe (13.0).

*Anal.* Calc. for $C_{30}H_{33}O_6ClS$: C, 64.68; H, 5.97. Found: C, 64.71; H, 6.07.

O-(*3-O-Allyl-2,4,6-tri-O-benzyl-α-D-glucopyranosyl*)-(*1→3*)-*1,2,4,6-tetra-O-acetyl-β-D-glucopyranose* (**24**). — (*a*) The product obtained by treatment of a mixture of **8** (2.0 g, 5.7 mmol), **13** (3.74 g, 7.2 mmol), and powdered 4A molecular sieve (25 g) in ether (75 mL) and 1,2-dimethoxyethane (7 mL) with MeOTf (4.06 mL, 35.8 mmol), as described for the preparation of **17**, was subjected column chromatography (solvent *2*), to give **24** (2.87 g, 61%), $[\alpha]_D^{25}$ +39° (*c* 1.3, $CHCl_3$); $R_f$ 0.4 (t.l.c. in solvent *4*); $^{13}$C-n.m.r. ($CDCl_3$): $\delta$ 170.3, 169.3 (2 C), and 168.9 (C=O), 138.9, 138.1, and 138.0 (aromatic C-1), 135.2 and 116.4 ($CH=CH_2$), 99.6 (C-1′), 91.8 (C-1), and 20.8, 20.7 (2 C), and 20.6 ($COCH_3$).

*Anal.* Calc. for $C_{44}H_{52}O_{15}$: C, 64.38; H, 6.39. Found: C, 64.52; H, 6.46.

(*b*) A mixture of $CuBr_2$ (1.25 g, 5.6 mmol), $Bu_4NBr$ (0.36 g, 1.1 mmol), and powdered 4A molecular sieve (3 g) in 1,2-dichloroethane (10 mL) and *N,N*-dimethylformamide (3 mL) was treated with a solution of **8** (1.0 g, 2.9 mmol) and **13**

(1.94 g, 3.7 mmol) in 1,2-dichloroethane (5 mL) as described for the preparation of **17**. The mixture was stirred overnight at room temperature, at which time t.l.c. (solvent *4*) showed the disappearance of **13** ($R_F$ 0.81) and the presence of two major [$R_F$ 0.79 and 0.38 (**21**)] and two minor components ($R_F$ 0.77 and 0.33), together with unchanged **8** ($R_F$ 0.06). Processing of the mixture as described for the preparation of **17**, followed by column chromatography of the product as in (*a*), gave **24** (1.13 g, 48%).

An attempt to isolate purely the product ($R_F$ 0.79) by column chromatography failed.

O-(*2,4,6-Tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→3*)-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**25**). — A mixture of **24** (3.40 g), $PdCl_2$ (0.77 g), and NaOAc (3 g) in AcOH–$H_2O$ (20:1, 31.5 mL) was stirred overnight at room temperature. Insoluble material was collected on a Celite pad and washed with MeOH, and the combined filtrate and washings were evaporated. A solution of the residue in $CH_2Cl_2$ was washed successively with $H_2O$, aq. $NaHCO_3$, and $H_2O$, dried, and evaporated. Column chromatography (solvent *3*) of the residue gave **25** (2.68 g, 83%), $[\alpha]_D^{25}$ +59° (*c* 1.6, $CHCl_3$); $R_F$ 0.32 (t.l.c. in solvent *5*); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.4, 169.2, 169.0, and 168.9 (C=O), 138.45, 137.9, and 137.8 (aromatic C-1), 98.6 (C-1′), 91.8 (C-1), and 20.7 and 20.6 ($COCH_3$).

*Anal.* Calc. for $C_{41}H_{48}O_{15}$: C, 63.07; H, 6.20. Found: C, 63.20; H, 6.30.

O-(*2,3,4,6-Tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→3*)-*bis*[O-(*2,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→3*)]-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**26**). — The product obtained by treatment of a mixture of **25** (0.43 g, 551 μmol), $CuBr_2$ (0.24 g, 1.1 mmol), $Bu_4NBr$ (0.17 g, 527 μmol), and powdered 4A molecular sieve (2 g) in 1,2-dichloroethane (5 mL) and *N,N*-dimethylformamide (1 mL) with **21** (0.72 g, 718 μmol), as described for the preparation of **22**, was subjected to column chromatography, to give **26** (0.61 g, 64%), $[\alpha]_D^{25}$ +68.5° (*c* 1.0, $CHCl_3$); $R_F$ 0.36 (t.l.c. in solvent *4*); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.3, 169.1, and 168.9 (C=O), 138.7-137.7 (aromatic C-1), 99.0 (C-1‴), 97.1 (C-1′), 95.5 (C-1″), 91.8 (C-1), and 20.8, 20.6, and 20.3 ($COCH_3$).

*Anal.* Calc. for $C_{102}H_{110}O_{25}$: C, 70.57; H, 6.39. Found: C, 70.67; H, 6.51.

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→3*)-*bis*[O-(*2,4,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→3*)]-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**27**). — Hydrogenolysis of **26** (0.49 g) and acetylation, followed by purification of the product as described for the preparation of **18**, afforded **24** (0.32 g, 91%), $[\alpha]_D^{25}$ +114° (*c* 1.1, $CHCl_3$); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.5–168.5 (C=O), 95.8 (C-1‴), 95.4 (C-1′), 95.1 (C-1″), 91.8 (C-1), and 20.7 ($COCH_3$).

*Anal.* Calc. for $C_{52}H_{70}O_{35}$: C, 49.76; H, 5.62. Found: C, 49.70; H, 5.70.

O-α-D-*Glucopyranosyl*-(*1→3*)-*bis*[O-α-D-*glucopyranosyl*-(*1→3*)]-D-*glucopyranose* (**3**).— *O*-Deacetylation of **27** (215 mg), as described for the preparation of **1**, gave **3** (107 mg, 94%), $[\alpha]_D^{25}$ +201° (*c* 0.6, $H_2O$); lit.[5] $[\alpha]_D$ +205° ($H_2O$); $R_{Glc}$ 2.275 (l.c.); $^{13}$C-n.m.r. ($D_2O$): δ 101.8 (3 C, C-1′,1″,1‴), 98.5 (C-1β), 94.8 (C-1α), 85.0 and 82.5 (C-3), 82.7 (2 C, C-3′,3″), 78.2, 75.5, 74.3, 74.2, 73.8, 72.9, 72.7, 72.5, 72.1, and 63.3 and 63.0 (C-6,6′,6″,6‴).

*Anal.* Calc. for $C_{24}H_{42}O_{21}$: C, 43.25; H, 6.35. Found: C, 43.38; H, 6.48.

O-(*3*-O-*Allyl-2,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1*→*3*)-O-(*2,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**28**). — The product obtained by treatment of a mixture of **25**. (1.02 g, 1.3 mmol), **13** (0.88 g, 1.7 mmol), and powdered 4A molecular sieve (5 g) in ether (20 mL) with MeOTf (0.74 mL, 6.5 mmol), as described previously, was subjected to column chromatography (solvent *3*), to give **28** (0.97 g, 59%); $[\alpha]_D^{25}$ + 59° (*c* 1.5, $CHCl_3$): $R_F$ 0.38 (t.l.c. in solvent *4*); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.4, 169.0, and 168.9 (C=O), 138.6-137.75 (aromatic C-1), 135.3 and 116.2 ($CH{=}CH_2$), 98.7 (C-1″), 97.0 (C-1′), 91.9 (C-1), and 20.8, 20.7, and 20.4 ($COCH_3$).

*Anal.* Calc. for $C_{71}H_{80}O_{20}$: C, 68.04; H, 6.43. Found: C, 68.31; H, 6.55.

O-(*2,4,6-Tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1*→*3*)-O-(*2,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1*→*3*)-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**29**). — A mixture of **28** (0.78 g), $PdCl_2$ (0.12 g), and NaOAc (0.56 g) in AcOH–$H_2O$ (20:1, 8.4 mL) was stirred overnight at room temperature. Processing of the mixture, followed by column chromatography (solvent *3* )of the product as described for the preparation of **25**, gave **29** (0.61 g, 80%), $[\alpha]_D^{25}$ + 65°(*c* 1.2, $CHCl_3$); $R_F$ 0.47 (t.l.c. in solvent *5*); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.4, 169.1, and 168.9 (C=O), 138.6–137.75 (aromatic C-1), 98.8 (C-1″), 96.4 (C-1′), 91.9 (C-1), and 20.8, 20.7, and 20.45 ($COCH_3$).

*Anal.* Calc. for $C_{68}H_{76}O_{20}$: C, 67.31; H, 6.31. Found: C, 67.48; H, 6.25.

O-(*2,3,4,6-Tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1*→*3*)-*tris*[O-*2,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1*→*3*)]-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**30**). — The product obtained by treatment of a mixture of **29** (0.71 g, 585 μmol), $CuBr_2$ (0.24 g, 1.1 mmol), $Bu_4NBr$ (0.17 g, 775 μmol), and powdered 4A molecular sieve (2 g) in 1,2-dichloroethane (5 mL) and *N*,*N*-dimethylformamide (1 mL) with **21** (0.73 g, 728 μmol), as described previously, was subjected to column chromatography (solvent *3*), to give **30** (0.75 g, 59%), $[\alpha]_D^{25}$ + 76° (*c* 1.2, $CHCl_3$); $R_F$ 0.3 (t.l.c. in solvent *4*); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.7, 169.4, 169.2, and 169.0 (C=O), 138.7-137.7 (aromatic C-1), 99.15 (C-1‴), 97.2 (C-1′), 95.9 (C-1‴), and 95.6 (C-1″), 91.9 (C-1), and 20.8, 20.7, and 20.3 ($COCH_3$).

*Anal.* Calc. for $C_{129}H_{138}O_{30}$: C, 71.45; H, 6.41. Found: C, 71.61; H, 6.58.

O-(*2,3,4,6-Tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*3*)-*tris*[O-(*2,4,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1*→*3*)]-*1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**31**). — Hydrogenolysis of **30** (0.61 g), followed by acetylation and column chromatography of the product, as described for the preparation of **18**, gave **31** (0.38 g, 88%), $[\alpha]_D^{25}$ + 119° (*c* 1.1, $CHCl_3$); $^{13}$C-n.m.r. ($CDCl_3$): δ 170.4–168.5 (C=O), 95.8 (C-1⁗), 95.5 (C-1′), 95.1 and 95.0 (C-1″,1‴) 91.8 (C-1), and 20.8 and 20.7 ($COCH_3$).

*Anal.* Calc. for$C_{64}H_{86}O_{43}$: C, 49.81; H, 5.62. Found: C, 50.01; H, 5.70.

O-α-D-*Glucopyranosyl*-(*1*→*3*)-*tris*[O-α-D-*glucopyranosyl*-(*1*→*3*)]-D-*glucopyranose* (**4**). — *O*-Deacetylation of **31** (215 mg), as described for the preparation of **1**, gave **4** (109 mg, 95%), $[\alpha]_D^{25}$ + 221° (*c* 0.9, $H_2O$); lit.[5] $[\alpha]_D$ + 223° ($H_2O$); $R_{Glc}$ 3.02 (l.c.); $^{13}$C-n.m.r. ($D_2O$): δ 102.0 (2 C) and 101.8 (2 C) (C-1′, 1″, 1‴, 1⁗), 98.6 (C-1β), 94.9 (C-1α), 85.1 and 82.6 (C-3), 82.8 (3 C, C-3′, 3″, 3‴), 78.3, 75.6, 74.4, 74.3, 73.8, 73.05, 72.5, 72.2, and 63.3 and 63.1 (C-6,6′,6″, 6‴, 6⁗).

*Anal.* Calc. for $C_{30}H_{52}O_{26}$: C, 43.48; H, 6.32. Found: C, 43.37; H, 6.50.

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