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Note

Convenient synthesis of a building-block derivative of nigerose*

BOGDAN DOBOSZEWSKI† AND ALEKSANDER ZAMOJSKI
Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw (Poland)
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Fragments having the structure of nigerose [**1**, α-D-Glc*p*(1→3)-D-Glc*p*] occur in various oligo- and poly-saccharides[1]. The synthesis of **1** has been accomplished in several ways[2–8]. However, for the synthesis of a pentasaccharide from the *Shigella sonnei* outer-core oligosaccharide[9] (incorporating disaccharide **1**), it was necessary to elaborate a new approach to a derivative of **1** suitable as a glycosylating agent.

The reducing part of the disaccharide was obtained from penta-*O*-acetyl-β-D-glucopyranose (**2**) in the following way. The reaction of **2** with 2,2,2-trichloroethanol plus tin tetrachloride as a catalyst[10] smoothly gave a 76% yield of a mixture of anomeric glucosides **3**. The mixture was deacetylated and benzylidenated *in situ* to 4,6-*O*-benzylidene derivatives (83% yield), which were separated by chromatography into pure α and β anomers (**4** and **5**) in the approximate ratio 1:2. For further transformation, only **5** was subjected to phase-transfer etherification, which with diols of type **4** or **5** is known to furnish 2-*O*-alkylated derivatives in predominance[11]. The reaction of **5** with a limited amount of allyl bromide in the dichloromethane–10% aqueous sodium hydroxide system in the presence of tetra-*n*-butylammonium bromide as the catalyst gave two regioisomeric mono-*O*-allylated derivatives **6** (72%) and **7** (12%), which were separated by chromatography.

Position of the alkyl group could be deduced from the chemical shift of H-1 (δ 4.66 for **6**, 4.35 for **7**). A low-field shift for **6** can be explained by the presence of the allyloxy grouping next to the anomeric proton. This assignment was further substantiated by the ^{1}H-n.m.r. spectra of acetylated **6** and **7**, compounds **8** and **9**, respectively (see Experimental).

Analogous phase-transfer benzylation of **5** furnished two mono-*O*-benzylated derivatives **10** (59%) and **11** (13%). Here again the position of the benzyl group could be inferred from the differences in chemical shift of protons in the vicinity of the benzyloxy groups: δ 4.81 and 4.66 for H-1 in **10** and **11**, and, correspondingly,

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†Present address: University of California, Department of Botany, Berkeley, California 94720, U.S.A.

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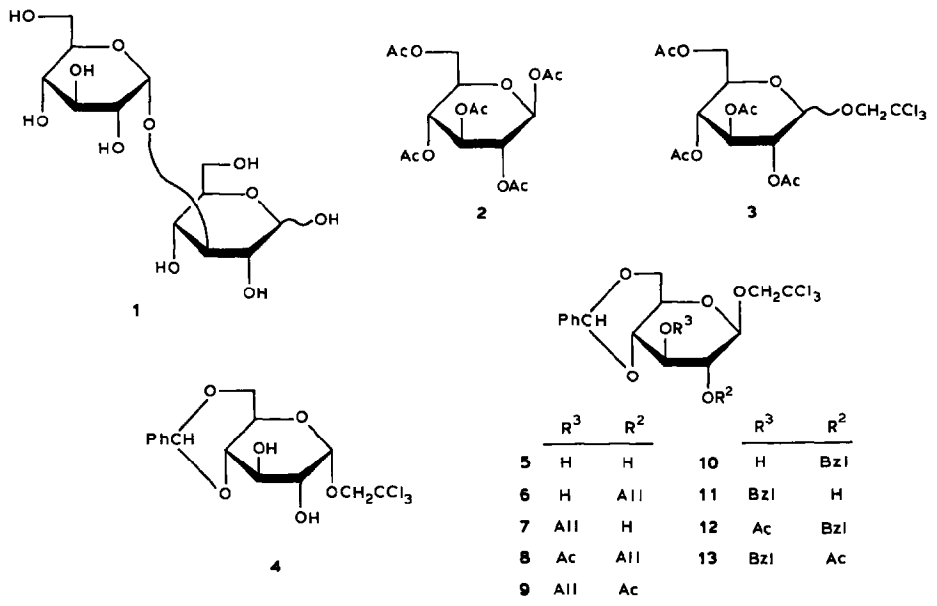


	R^3	R^2		R^3	R^2
5	H	H	10	H	Bzl
6	H	All	11	Bzl	H
7	All	H	12	Ac	Bzl
8	Ac	All	13	Bzl	Ac
9	All	Ac			

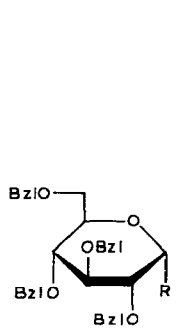
δ 5.45 and 5.56 for PhC*H*, and δ 4.40 and 4.28 for CH_2CCl_3, thus indicating **10** to be the 2-*O*-benzyl derivative. The assignment was further corroborated by the ^{1}H-n.m.r. data for the acetylated derivatives **12** and **13**.

For the condensation of **6** with 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl chloride (**14**) we employed first the proven Helferich method[12]. The reaction of **6** with a double-molar amount of **14** in the presence of mercuric cyanide gave the α-bonded disaccharide **16** in 35% yield as the sole product. However, the reaction of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**15**) with **6** in the presence of tetraethylammonium bromide[13] gave an increased yield (46%) of **16**. When a fourfold molar excess of **15** was taken, the yield of **16** further increased to 80%. As a side-product in the reactions with **15** a certain amount of 1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-D-*arabino*-hex-1-enitol (**18**) was isolated. A condensation of **14** with **6** under phase-transfer conditions, with 18-crown-6 as the catalyst and 50% aqueous potassium hydroxide as the second phase (or solid potassium hydroxide or solid potassium carbonate), gave **16** in only ~25% yield. Some formation of **18** was also noticed.

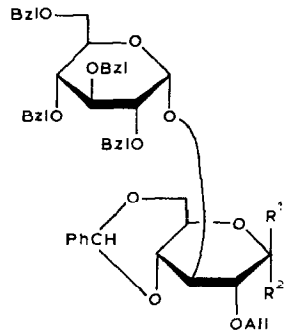
The α configuration of the intersugar bond in **16** was inferred from the ^{13}C-n.m.r. shift of C-1′ (96.01 p.p.m.).

The aglycon in the reducing part of **16** could be readily removed with zinc and 2,4-pentanedione[14] to give **17** in 85% yield, thus furnishing a nigerose derivative ready for glycosidation.

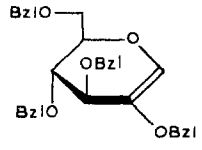
Disaccharide **16**, having selectively removable groups in the reducing part, is also particularly suitable as the aglycon partner in the synthesis of branched-chain oligosaccharides.



14 R = Cl
15 R = Br



16 R^1 = OCH_2CCl_3, R^2 = H
17 R^1, R^2 = H, OH



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EXPERIMENTAL

N.m.r. spectra were recorded at 100 MHz for solutions in $CDCl_3$ (internal Me_4Si), unless otherwise indicated. Optical rotations were measured at 19 ±1°. Other general methods were as described before[15].

*2,2,2-Trichloroethyl 2,3,4,6-tetra-*O*-acetyl-α/β-*D*-glucopyranoside* (**3**). — To a solution of **2** (16 g) and 2,2,2-trichloroethanol (8 mL) in dichloromethane (60 mL) was added stannic chloride (6 mL). The mixture was kept overnight at room temperature, diluted with chloroform, washed with water, dried, and concentrated under vacuum. The residue was then purified on a silica gel column. Elution with 9:1 hexane–acetone removed the excess 2,2,2-trichloroethanol. Product **3** (15 g, 76%) was eluted from the column with acetone. A few fractions containing the pure α and pure β anomers, respectively, were obtained at the beginning and end of the elution. Isolated, pure α anomer had m.p. 97–98° (from hexane–ether), $[\alpha]_D$ +135° (*c* 1, chloroform); lit.[16] m.p. 99–100°, $[\alpha]_D$ +136° (chloroform); and the β anomer had m.p. 141–142°, $[\alpha]_D$ −25° (*c* 1, chloroform); lit.[16] m.p. 143–144°, $[\alpha]_D$ −24° (chloroform).

*2,2,2-Trichloroethyl 4,6-*O*-benzylidene-α- and -β-*D*-glucopyranosides* (**4** *and* **5**). — To a solution of **3** (15 g) in methanol (250 mL) was added triethylamine (20 mL). After overnight standing at room temperature the solution was concentrated under vacuum to dryness. Benzaldehyde (30 mL) and zinc chloride (8 g) were added and the flask was shaken for 3 days. The mixture was poured into water and extracted with chloroform. The chloroform solution was dried and concentrated to leave an oily residue. Chromatography (3:1 hexane–ethyl acetate) gave **5** (6.86 g, 55%), m.p. 100–103° (from hexane–ether), $[\alpha]_D$ −3° (*c* 4, chloroform); ^{1}H-N.m.r.: δ 5.50 (s, 1 H, PhC*H*), 4.59 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.31 (dd, 1 H, $J_{6e,5}$ 4.0, $J_{6e,6a}$ 10.0 Hz, H-6e), 4.27 (q_{AB}, 2 H, CH_2CCl_3), and 3.07–3.92 (m, 7 H, H-2,3,4,5,6a, and 2 O*H*); ^{13}C-n.m.r.: δ 103.53 (C-1), 74.42 (C-2), 72.95 (C-3), 80.24 (C-4, CH_2CCl_3), 66.60 (C-5), 68.45 (C-6), 101.91 (PhCH), and 96.06 (CH_2CCl_3).

Anal. Calc. for $C_{15}H_{17}Cl_3O_6$: C, 45.1; H, 4.3; Cl, 26.6. Found: C, 44.8; H, 4.3; Cl, 26.6.

Eluted second was **4** (3.51 g, 28%), m.p. 109.5–111° (from hexane–ether), $[\alpha]_D$ +91° (*c* 1, chloroform); ^{1}H-n.m.r.: δ 5.50 (s, 1 H, PhC*H*), 5.09 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.01–4.35 (m, 3 H, CH_2CCl$_3$, H-6e), and 3.36–4.08 (m, 5 H, H-2,3,4,5,6a); ^{13}C-n.m.r.: δ 99.78 (C-1), 72.65 (C-2), 71.13 (C-3), 79.68, 80.58 (C-4, CH_2CCl$_3$), 63.46 (C-5), 68.57 (C-6), 101.82 (PhCH), and 95.97 (CH$_2$CCl$_3$).

Anal. Found: C, 45.0; H, 4.0; Cl, 26.5.

*2,2,2-Trichloroethyl 2-O-allyl- and 3-O-allyl-4,6-O-benzylidene-β-*D*-glucopyranosides* (**6** *and* **7**). — To a solution of **5** (6 g, 14 mmol) in dichloromethane (150 mL) were added allyl bromide (2.1 g, 17.4 mmol), tetra-*n*-butylammonium bromide (1.14 g), and 10% aqueous sodium hydroxide (15 mL), and the mixture was shaken at room temperature. After 8 h the organic phase was separated, dried, and concentrated to dryness. The residue, composed of two components (R_F 0.83 and 0.78 in 1:1 hexane–ethyl acetate) was flash chromatographed with 3:1 hexane–ethyl acetate. Eluted first was **7** (0.79 g, 12%), m.p. 129–131° (from hexane–ether), $[\alpha]_D$ −40° (*c* 0.7, chloroform); ^{1}H-n.m.r.: δ 5.53 (s, 1 H, PhC*H*), 4.35 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 4.32 (q_{AB}, 2 H, CH_2CCl$_3$), 4.15–4.79 (m, 3 H, CH_2CH=CH$_2$, H-6e), 3.28–3.93 (m, 5 H, H-2,3,4,5,6a), 5.90 (m, 1 H, CH$_2$C*H*=CH$_2$), 5.17, and 5.30 (2 m, 2 H, CH$_2$CH=CH_2); ^{13}C-n.m.r.: δ 103.75 (C-1), 74.06 (C-2), 80.95, 80.73, 79.59 (C-3, 4 and CH_2CCl$_3$), 66.59 (C-5), 68.43 (C-6), 101.21 (PhCH), 96.01 (CH$_2$CCl$_3$), 73.58, 117.25, and 134.8 (CH_2CH=CH$_2$).

Anal. Calc. for $C_{18}H_{21}Cl_3O_6$: C, 49.2; H, 4.8; Cl, 24.2. Found: C, 49.0; H, 4.7; Cl, 24.3.

Eluted second was **6** (4.73 g, 72%), m.p. 118–120° (from hexane–ether), $[\alpha]_D$ −47° (*c* 2.4, chloroform); ^{1}H-n.m.r.: δ 5.48 (s, 1 H, PhC*H*), 4.66 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.28 (q_{AB}, 2 H, CH_2CCl$_3$), 4.11–4.60 (m, 3 H, CH_2CH=CH$_2$, H-6e), 3.21–3.89 (m, 5 H, H-2,3,4,5,6a), 5.94 (m, 1 H, CH$_2$C*H*=CH$_2$), 5.17, and 5.28 (2 m, 2 H, CH$_2$CH=CH_2); ^{13}C-n.m.r.: δ 104.00 (C-1), 80.90, 81.03 (C-2 and CH_2CCl$_3$), 72.87 (C-3), 80.22 (C-4), 66.34 (C-5), 68.49 (C-6), 101.81 (PhCH), 73.77, 117.85, 134.60 (CH_2CH=CH$_2$), and 96.03 (CH$_2$CCl$_3$).

Anal. Found: C, 49.0; H, 4.8; Cl, 24.3.

*2,2,2-Trichloroethyl 3-O-acetyl-2-O-allyl-4,6-O-benzylidene-β-*D*-glucopyranoside* (**8**). — This was obtained by the acetylation of **6** with Ac_2O and pyridine, m.p. 186–187.5° (from ethanol), $[\alpha]_D$ −61° (*c* 4, chloroform); ^{1}H-n.m.r. (C_6D_6): δ 5.46 (t, 1 H, $J_{2,3}$ and $J_{3,4}$ 9.4 Hz, H-3), 5.21 (s, 1 H, PhC*H*), 4.31 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 3.96 (q_{AB}, 2 H, CH_2CCl$_3$), 3.98–4.61 (m, 3 H, CH_2CH=CH$_2$, H-6e), 2.96–3.54 (m, 4 H, H-2,4,5,6a), 1.80 (s, 3 H, COCH_3), 5.86 (m, 1 H, CH$_2$C*H*=CH$_2$), 5.05, and 5.25 (2 m, 2 H, CH$_2$CH=CH_2).

Anal. Calc. for $C_{20}H_{23}Cl_3O_7$: C, 49.9; H, 4.8; Cl, 22.1. Found: C, 49.8; H, 4.8; Cl, 22.0.

*2,2,2-Trichloroethyl 2-O-acetyl-3-O-allyl-4,6-O-benzylidene-β-*D*-glucopyranoside* (**9**). — The acetylation of **7** gave **9**, m.p. 147–148° (from hexane–ether), $[\alpha]_D$

−53° (*c* 1.2, chloroform); ^{1}H-n.m.r. (C_6D_6): δ 5.30 (t, 1 H, $J_{1,2} \approx J_{2,3}$ ~7.9 Hz, H-2), 5.17 (s, 1 H, PhC*H*), 4.39 (d, 1 H, H-1), 4.08 (dd, 1 H, $J_{6a,6e}$ 10.3, $J_{6e,5}$ 4.6 Hz, H-6e), 3.68–4.34 (q_{AB} and m, 4 H, $CH_2CH{=}CH_2$ and CH_2CCl_3), 2.91–3.65 (m, 4 H, H-3,4,5,6a), 5.82 (m, 1 H, $CH_2CH{=}CH_2$), 5.03, and 5.24 (2 m, 2 H, $CH_2CH{=}CH_2$), 1.88 (s, 3 H, $COCH_3$).

Anal. Found: C, 49.6; H, 4.8; Cl, 21.8.

*2,2,2-Trichloroethyl 2-O-benzyl- and 3-O-benzyl-4,6-O-benzylidene-β-*D*-glucopyranosides* (**10** *and* **11**). — To a solution of **5** (3 g) in dichloromethane (80 mL), benzyl bromide (1.1 mL), tetra-*n*-butylammonium bromide (0.65 g), and 10% aqueous sodium hydroxide (8 mL) were added. After the mixture was shaken for 8 h the aqueous phase was exchanged for a fresh portion and the reaction was continued for an additional 5 h. Separation of the organic phase, drying, and concentration to dryness gave a mixture of two products which were separated by flash chromatography (3:1 hexane–ethyl acetate). Eluted first was **11** (0.48 g, 13%), m.p. 101.5–102.5° (from hexane–ether), $[\alpha]_D$ −39° (*c* 1.6, chloroform); ^{1}H-n.m.r.: δ 5.56 (s, 1 H, PhC*H*), 4.88 (q_{AB}, 2 H, $PhCH_2$), 4.66 (d, 1 H, $J_{1,2}$ 6.8 Hz, H-1), 4.34 (dd, 1 H, $J_{6e,6a}$ 10.0, $J_{6e,5}$ 4.5 Hz, H-6e), 4.28 (q_{AB}, 2 H, CH_2CCl_3), and 3.30–3.92 (m, 5 H, H-2,3,4,5,6a).

Anal. Calc. for $C_{22}H_{23}Cl_3O_6$: C, 54.0; H, 4.7; Cl, 21.7. Found: C, 53.8; H, 5.0; Cl, 21.7.

Eluted second was **10** (2.17 g, 59%), m.p. 120–121.5° (from hexane–ether), $[\alpha]_D$ −27° (*c* 1, chloroform); ^{1}H-n.m.r.: δ 5.45 (s, 1 H, PhC*H*), 4.99 (q_{AB}, 2 H, $PhCH_2$), 4.81 (d, 1 H, $J_{1,2}$ 6.8 Hz, H-1), 4.40 (q_{AB}, 2 H, CH_2CCl_3), 4.39 (dd, 1 H, $J_{6e,6a}$ 10.3, $J_{6e,5}$ 4.6 Hz, H-6e), and 3.28–3.90 (m, 5 H, H-2,3,4,5,6a).

Anal. Found: C, 54.0; H, 4.8; Cl, 21.8.

*2,2,2-Trichloroethyl 3-O-acetyl-2-O-benzyl-4,6-O-benzylidene-β-*D*-glucopyranoside* (**12**) — Conventional acetylation of **10** gave **12**, m.p. 110–112° (from hexane–ether), $[\alpha]_D$ −27° (*c* 1.6, chloroform); ^{1}H-n.m.r. (C_6D_6): δ 5.52 (t, 1 H, $J_{2,3}$ and $J_{3,4}$ 9.3 Hz, H-3), 5.22 (s, 1 H, PhC*H*), 4.83 (q_{AB}, 2 H, $PhCH_2$), 4.38 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.09 (dd, 1 H, $J_{6e,6a}$ 9.5, $J_{6e,5}$ 4.0 Hz, H-6e), 3.96 (q_{AB}, 2 H, CH_2CCl_3), 3.45 (dd, 1 H, H-2), 3.03–3.52 (m, 3 H, H-4,5,6a), and 1.73 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{24}H_{25}Cl_3O_7$: C, 54.2; H, 4.7; Cl, 20.0. Found: C, 54.2; H, 4.7; Cl, 20.0.

*2,2,2-Trichloroethyl 2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-β-*D*-glucopyranoside* (**13**). — Compound **11** similarly gave **13**, m.p. 132–134° (from hexane–ether), $[\alpha]_D$ −22° (*c* 1.3, chloroform); ^{1}H-n.m.r. (C_6D_6): δ 5.35 (t, 1 H, $J_{2,1} \approx J_{2,3}$ ~8.0 Hz, H-2), 5.20 (s, 1 H, PhC*H*), 4.75 (q_{AB}, 2 H, $PhCH_2$), 4.32 (d, 1 H, H-1), 4.09 (dd, 1 H, $J_{6e,6a}$ 10.5, $J_{6e,5}$ 5.0 Hz, H-6), 3.96 (q_{AB}, 2 H, CH_2CCl_3), 2.90–3.63 (m, 4 H, H-3,4,5,6a), and 1.84 (s, 3 H, $COCH_3$).

Anal. Found: C, 54.0; H, 4.7; Cl, 20.1.

*2,2,2-Trichloroethyl 2-O-allyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**16**). — *A*. To a mixture of **6** (0.225 g)

and mercuric cyanide (0.252 g) in nitromethane (10 mL) a solution of **14** (ref. 17) (0.56 g) in benzene (10 mL) was added, and the mixture was stirred for 4 days at ~45°. Solvents were evaporated and the residual oil was chromatographed (4:1 hexane–ethyl acetate) to yield **16** (0.175 g, 35%) in the form of a glassy solid.

B. To a mixture of **6** (8.25 g), tetraethylammonium bromide (2.1 g), and powdered molecular sieves 4A (6 g) in dichloromethane (30 mL) was added a solution of **15** (ref. 13) (5.5 g) in dichloromethane (30 mL), and the reaction mixture was stirred at room temperature. After 7 days the solvent was evaporated and the resulting slurry was chromatographed with 4:1 hexane–ethyl acetate as eluant. First to emerge was **18** (0.55 g), m.p. 66–66.5°, $[\alpha]_D$ −7° (*c* 1, chloroform); lit.[18] m.p. 66–66.5°, $[\alpha]_D$ −5° (chloroform).

Eluted second was **16** (2.25 g, 46%), $[\alpha]_D$ +17° (*c* 2.6, chloroform); ^{13}C-n.m.r.: δ 104.42 (C-1), 81.88, 81.53, 80.84 (C-2,3, CH_2CCl_3), 79.49 (C-4), 65.84 (C-5), 69.70 (C-6,6′), 96.01 (C-1′, CH_2CCl_3), 78.63, 77.37, 75.59, 74.59, 71.17 (C-2′,3′,4′,5′, $PhCH_2$), 101.95 (PhCH), 73.34, 118.25, and 134.15 ($CH_2CH=CH_2$).

Anal. Calc. for $C_{52}H_{55}Cl_3O_{11}$: C, 64.9; H, 5.8. Found: C, 64.3; H, 5.9.

The condensation of **6** (0.11 g) as just described, but with a fivefold molar excess of bromide **15** (0.755 g), gave **16** (0.193 g, 80%).

C. To a solution of **14** (anomeric mixture of chlorides; 0.225 g) and **6** (0.11 g) in benzene (5 mL) were added 50% aqueous potassium hydroxide (2 mL) and a few crystals of 18-crown-6, and the two-phase system was vigorously stirred at 65°. After 2 days the organic layer was separated, dried, and concentrated to dryness. Chromatography of the residue gave small amounts of **18** and **16** (0.063 g, 26%). The use of solid potassium carbonate or potassium hydroxide for this condensation did not change the yield of **16** (25–26%).

2-O-Allyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α/β-D-glucopyranose (**17**). — The 2,2,2-trichloroethyl group in disaccharide **16** (0.5 g) was removed by the method of Adamiak[14] as described earlier[15] to give **17** (0.37 g, 85%), glassy solid, $[\alpha]_D$ +35° (*c* 1.4, chloroform).

Anal. Calc. for $C_{50}H_{54}O_{11}$: C, 72.3; H, 6.6. Found: C, 71.9; H, 6.5.

ACKNOWLEDGMENTS

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