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CARBOHYDRATE–UREA–PHENOL-BASED ADHESIVES: TRANSIENT FORMATION OF MONO- AND DI-D-GLUCOSYLUREA

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ABSTRACT

The chemistry of the acid stage of the synthesis of carbohydrate-based adhesives has been investigated. The sulfuric acid-catalyzed reactions of D-glucose with urea in a phenol–water solution provided both *N*-β-D-glucopyranosylurea and *N,N'*-di-β-D-glucopyranosylurea. These compounds have been isolated from the resin as perbenzoylated derivatives, and compared spectroscopically with authentic samples. The D-glucosylureas are transient products whose combined yields approach 35% of the carbohydrate fraction during the initial stages of resin synthesis. Only traces of 5-(hydroxymethyl)-2-furaldehyde, levulinic acid, and formic acid were detected in the resin mixture, suggesting that the classical dehydration pathway is not a major route for the disappearance of D-glucose.

INTRODUCTION

The forest products industry is currently interested in decreasing the amount of phenol required to formulate adhesives designed for exterior use. Previous studies[1,2] indicated that the substitution of D-glucose or starch for a substantial amount of the phenol produces an adhesive having excellent strength properties.

The use of carbohydrates in adhesive formulations typically involves a two-stage process[3]. During the first stage, a carbohydrate is allowed to react with urea in an acidified phenol–water solution. The approximate molar ratios of carbohydrate–urea–phenol–water are typically 2:1:2:2. The relatively low proportion of water (5.7% by wt.) provides a viscous solution that is a solid at room temperature. The mixture is stirred at 90° until it is homogeneous, and the reaction is initiated by the addition of a small amount of sulfuric acid (0.7% by wt.). A 3–4-h reaction at temperatures up to 135–140° completes the acid stage, during which time, water and a portion of the phenol are removed as distillate.

The chemistry occurring during the resin synthesis is not yet understood, and we have begun characterization of the process by studying the first reaction stage, with D-glucose as the model carbohydrate. A considerable proportion of the avail-

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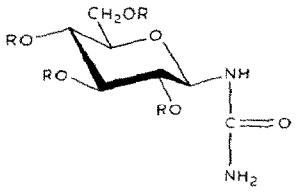
able D-glucose has been observed to react with urea to form both *N*-β-D-glucopyranosylurea (**1**) and *N,N'*-di-β-D-glucopyranosylurea (**3**). These compounds were isolated from the resin mixture as their respective perbenzoylated derivatives (**2** and **4**) through preparative high-performance liquid chromatography (h.p.l.c.). Because the spectroscopic properties of compounds **1–4** had not been reported in the literature, this information is presented as well.



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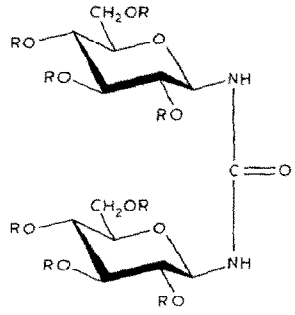
2 R = Bz



3 R = H
4 R = Bz

RESULTS AND DISCUSSION

The synthetic preparations of **1** and **3** were originally described by Schoorl[4,5], and several minor modifications have since appeared[6–9]. The procedure of Benn and Jones[9] was chosen in this work for the preparation of standard material, because it is by far the most convenient. The sulfuric acid-catalyzed reaction of an excess of urea with D-glucose for 42 h at 70° provided a 14% overall yield of crystalline **1**. A limiting amount of urea for 24 h at 70° provided crystalline **3** in 16% overall yield. Higher yields can be obtained by the use of longer reaction times (7–14 days), indicating the slow kinetic nature of D-glucosylurea formation.

In general, ureide linkages are stable toward acid hydrolysis relative to glycosylamines and *N*-alkylglycosylamines. Thus, Amadori rearrangement reactions and D-glucosylurea anomerization have not been observed[10,11]. Storage of synthetic **1** and **3** over a desiccant, or in dilute aqueous solution, for at least 6 months has led to no detectable chemical decomposition or change.

As might be expected, the acid-catalyzed interaction of D-glucose, urea, and phenol provided an extremely dark and viscous product. Quantitative determination of the yields of D-glucosylurea necessitated fractionation of this material. Although the colored reaction-products are probably an extremely complex mixture, their formation could be quite important for the development of the resin properties observed. Quantitative separation and isolation of the carbohydrates

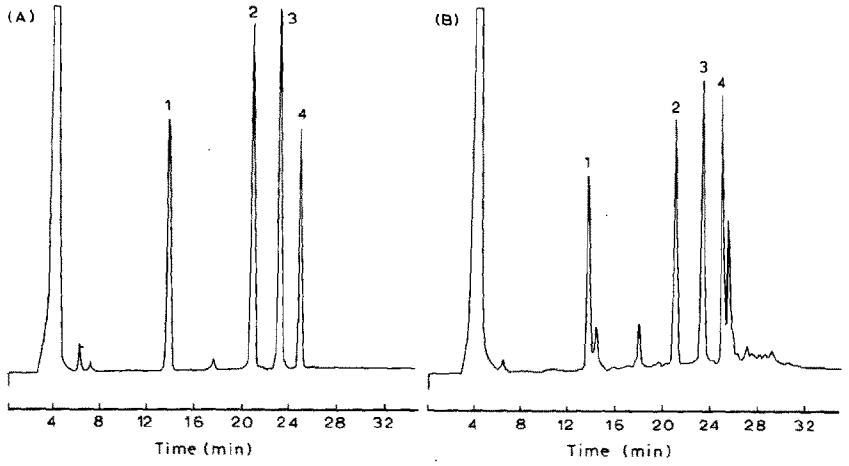


Fig. 1. Analytical h.p.l.c. separations of perbenzoylated carbohydrates: **1A**, standard mixture; **1B**, carbohydrate fractions of the acid-stage resin. Key: 1, mono-D-glucosylurea tetrabenzoate; 2, pentaerythritol tetrabenzoate; 3, D-glucose pentabenzoate; 4, di-D-glucosylurea octabenzoate. See Experimental for separation conditions.

and dark-colored reaction-products were achieved with the use of polystyrene–divinylbenzene (PS–DVB), high-porosity, copolymeric beads (Diaion HP20). The non-aromatic carbohydrate fraction passed unretained through the hydrophobic HP20 material with use of water as the eluant. The extremely dark, and presumably non-polar, aromatic reaction-products were retained within the polymeric network *via* an adsorption phenomenon. A simple ethanol wash quantitatively eluted the dark fraction from the beads (>96% recovery). The water and ethanol eluates are respectively referred to as the carbohydrate and resin precursor fractions. PS–DVB porous polymer beads are an attractive alternative to activated charcoal, because the colored degradation-products can be easily obtained for further study.

Quantification of the carbohydrate fraction. — All attempts to separate the resin-derived carbohydrate fraction in the underivatized form by h.p.l.c. resulted in poor resolution and variable retention-times. An experimental survey of the more common derivatization techniques[12,13] revealed that an excellent separation of the carbohydrate fraction could be achieved with the perbenzoylated derivatives. Esterification was effected with benzoic anhydride in pyridine by using 4-(dimethylamino)pyridine (DMAP) as the catalyst[14]. The moderate reaction conditions (4 h at room temperature) decreased the possibility of altering unstable resin reaction-products while increasing the detection capabilities of the analytical h.p.l.c. system.

Examples of the perbenzoate h.p.l.c. separations may be seen in Fig. 1. Excellent separation of a standard synthetic mixture is achieved by gradient elution on a C-8 analytical column (see Fig. 1A). Compound **1** contains a free $CONH_2$ group, and is therefore eluted first. A combination of molecular size and polarity determines the retention times of the other standard perbenzoates. The perbenzoylated resin carbohydrate fraction is slightly more complicated (see Fig. 1B); several unknowns are present.

The composition of the carbohydrate fraction as a function of reaction time and temperature is presented in Fig. 2. The values represent the percent by weight of the individual compounds with respect to the total weight of the carbohydrate fraction. There is an initial, rapid decrease in the amount of D-glucose present, with a concomitant increase in the amounts of **1** and **3**. While the temperature remained at 125°, the amounts of **1** and **3** present remained constant, whereas the amount of D-glucose continued to decrease. Although the thermostat was set to 140° at the beginning of the reaction, the temperature remained at 125° for ~80 min; it was during this period that most of the water and a portion of the phenol were distilled off. As the reaction temperature increased to 140°, the amount of **3** remained approximately the same, while those of **1** and D-glucose decreased.

That 30% of the carbohydrate fraction is composed of the D-glucosylureas indicates that these compounds contribute significantly to the chemistry of the acid stage. It was not possible to determine accurately the total yields of **1, 3,** and D-glucose as a function of the reaction time and temperature. The yields of **1, 3,** and D-glucose at the end of the reaction (on an initial D-glucose basis) were 5, 8, and 3%, respectively. While the final yields were low, the D-glucosylureas accounted for a larger proportion of the unused D-glucose in the initial stages of resin formation, and thereby acted as transient, and possibly important intermediates.

The presence of sulfuric acid and temperatures of 90–140° provide the conditions necessary for the decomposition of the D-glucose molecule by the dehydration

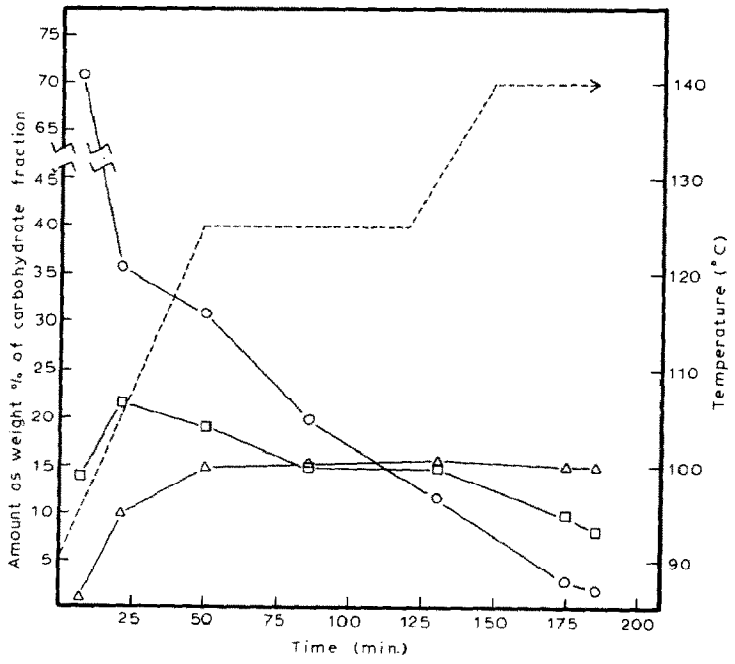


Fig. 2. Percent by weight of D-glucose (○), **1** (□), and **3** (△) present in the carbohydrate fraction (isolated from the PS-DVB beads) as a function of reaction time and temperature (-----).

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS FOR MONO- AND DI-D-GLUCOSYLUREAS (**1–4**)

Compound (solvent)	*Chemical shifts (p.p.m.)*						
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C=O*
1 (D_2O)	81.45	72.43	77.01	69.84	77.58	61.12	161.2
2 ($CDCl_3$)	80.66	71.50	73.27	69.59	73.65	63.17	157.5
3 (D_2O)	81.31	72.35	76.94	69.81	77.65	61.08	159.4
4 ($CDCl_3$)	80.84	71.45	72.93	69.38	73.57	63.12	155.4

pathway[15]. Indeed, Gibbons and Wondolowski[3] suggested that it is this reaction, *i.e.*, the formation of 5-(hydroxymethyl)-2-furaldehyde (HMF) from D-glucose, that provides the "monomer" that condenses with urea to form the acid-stage resin. However, if this reaction pathway contributes significantly to the overall acid-stage resin chemistry, it should have been possible to detect either HMF or its rehydration products, namely, levulinic acid and formic acid, in one of the separated fractions. H.p.l.c. analyses (organic acid column, HPX-87H) revealed only traces of the glucose dehydration products. This strongly suggests that classical dehydration leading to furans is not a major reaction-pathway for the degradation of D-glucose during resin synthesis. Instead, either another, as yet undetermined, route is utilized, or intermediates early in the dehydration pathway react with other components of the resin. It should be noted that at elevated temperatures, urea decomposes to form ammonia and cyanic acid[16].

Spectroscopic properties. — The spectroscopic properties of the glycosylamines[17,18] and perbenzoylated carbohydrates[19,20] have been reported, but those of **1–4** have not. The ^{13}C-n.m.r. data for compounds **1–4** are shown in Table I; as would be expected, the signal of the anomeric carbon atom is upfield of signals typical of D-glucosides. The assignments for compounds **1** and **3** were based on studies of the ^{1}H–^{13}C heteronuclear shift correlation.

The ^{1}H-n.m.r. chemical shifts and coupling constants are compiled in Table II. Assignments are based on 2D COSY experiments. The β-ureido linkage is preferred for both **1** and **3**, and both molecules assume the $^4C_1$ conformation. Perbenzoylation did not significantly affect the observed coupling constants (**1** *vs.* **2**, and **3** *vs.* **4**, respectively), and therefore derivatization does not alter the conformations of the D-glucosyl moieties.

The use of fast-atom bombardment-mass spectrometry (f.a.b.-m.s.) was helpful in confirming the structures of both the free and perbenzoylated D-glucosylureas. Cluster ions were detected in the mass spectra of **1** and **3** in both the positive- and negative-ion modes, as were ions corresponding to the intact molecules. The perbenzoate derivatives were characterized by molecular fragmentations typically associated with electron-impact ionization. An A-1 type of cleavage provided a tetra-*O*-benzoyl-D-glucosyl oxonium ion (*m/z* 579) in the positive-ion mode. The

TABLE II

^{1}H-N.M.R. CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR MONO- AND DI-D-GLUCOSYLUREAS (1–4)

Compound (solvent)	*Chemical shifts (p.p.m.)*								
	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6b*	*N–H*	*N–H$_2$*
1 (D_2O)	4.61d	3.17t	3.35t	3.21t	3.32m	3.53q	3.70q		
2 ($CDCl_3$)	5.53t	5.46t	6.03t	5.74t	4.28m	4.47q	4.62q	6.38d	5.11s
3 (D_2O)	4.70d	3.20t	3.36t	3.22t	3.34m	3.53q	3.70q		
4 (acetone-d_6)	5.76t	5.47t	6.15t	5.73t	4.50m	4.43bd	4.43bd	6.85d	
	Coupling constants (Hz)								
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	$J_{1,NH}$	
1	9.3	9.0	9.3	9.4	5.6	2.1	−12.4		
2	9.3	9.4	9.7	9.7	4.4	3.2	−12.2	8.6	
3	9.2	9.1	9.2	9.4	5.3	2.0	−12.3		
4	9.5	9.5	9.6	9.7	6.7	3.3		9.6	

loss of 1 or 2 molecules of benzoic acid was also observed in both the positive and negative modes.

Although the analytical h.p.l.c. system was originally developed to determine the yields of the D-glucosylureas as a function of reaction time and temperature, scale-up of the same system to the preparative size allowed the isolation of the D-glucosylureas from the resin mixture as their perbenzoylated derivatives. Spectroscopic characterization indicated that the synthetic and resin-derived materials were, indeed, identical.

CONCLUSION

N-β-D-Glucopyranosylurea (**1**) and *N,N*-'di-β-D-glucopyranosylurea (**3**) have been characterized spectroscopically. The perbenzoate derivatives of **1** and **3** have been isolated from the acid stage of the synthesis of a carbohydrate–urea–phenol-based adhesive. From this work, it has been determined that the major, initial, non-destructive reaction of D-glucose is the formation of the D-glucosylureas. Compounds **1** and **3** account for as much as 35% of the carbohydrate fraction isolated by chromatography on highly porous, copolymeric PS-DVB beads.

EXPERIMENTAL

General. — Melting points are uncorrected. All solvents were distilled prior to use. Evaporations were conducted under diminished pressure at 35–40°. Optical rotations at 589 nm were determined with a Perkin–Elmer 243 polarimeter.

Resin synthesis. — Phenol (14 g, loose crystals) and water (1.55 mL) were placed in a 100-mL, 3-necked, round-bottomed flask fitted with a short-path distilla-

tion head and receiver, a thermocouple, a temperature probe, and a thermistor temperature-controller probe. The mixture was heated to 90°, urea (4.5 g, 99.9%; Chemical Dynamics, South Plainfield, NJ) and D-glucose (27 g) were added, and the mixture was stirred until it became homogeneous (15 min); 2.5M H_2SO_4 (1.35 mL) was then added.

The temperature controller was set at 140°, and the reaction was allowed to proceed until 6 mL of distillate had accumulated in the receiving flask (185 min). The reaction was stopped by suspending the mixture in water (200 mL). The suspension was filtered, the filtrate mixed with pentaerythritol (as an internal standard), washed with ethyl acetate (2 × 200 mL), and the aqueous solution evaporated for a period sufficient to eliminate traces of ethyl acetate. The pH of the aqueous fraction was 8.5; it was adjusted to pH 6.5 by addition of dilute sulfuric acid.

The aqueous phase was made to 1 L with water, and an aliquot (100 mL) was submitted to a decolorizing step employing Diaion HP20 (donated by Mitsubishi Chemical Ind. Ltd., Tokyo). Prior to use, the beads were exhaustively cleaned with hot ethanol, to remove any ethanol-soluble impurities of low molecular weight, and were stored in the dry state. The beads (45 g) were dry-packed into a standard ion-exchange column, and activated with water (500 mL). The resin aliquot was eluted with water (300 mL) at the rate of ~5 mL/min; the carbohydrate fraction (1.6 g) was isolated by freeze-drying the eluate. The resin precursor fraction was isolated by eluting the column with 95% ethanol (300 mL). The ethanol fraction was evaporated to dryness, the residue dissolved in water, and the solution freeze-dried, to yield a dark-colored, fluffy, hygroscopic material (550 mg).

When the reaction time-course was being monitored, or h.p.l.c. standard samples were being prepared, the work-up procedure was the same, except that it was on a much smaller scale.

Perbenzoylation[14]. — The carbohydrate fraction (50 mg) was dissolved in water (50 mL), and an aliquot (1 mL) was freeze-dried in a 4-mL reaction-vial. The dried material was dissolved in 1 mL of freshly prepared benzoylation reagent [10% of benzoic anhydride plus 5% of DMAP (w/v) in pyridine]. After 4 h, the reaction was quenched by addition of water (100 μL). The solution was diluted with dichloromethane (10 mL), and washed with water (2 × 10 mL). Traces of pyridine were removed from the organic phase by three alternate additions and evaporations of toluene. The resulting solid was dissolved in acetonitrile, and the solution made to 10 mL for h.p.l.c. analysis.

D-Glucose and pentaerythritol perbenzoates were prepared according to the method of Fletcher[21].

High-performance liquid chromatography. — Analytical separations were performed with a Gilson System 45 (Middleton, WI) utilizing a column (4.6 × 250 mm; Phenomenex, Rancho Palos Verdes, CA) of Spherex C-8 (10 μm), and a matching guard-column. Detection was achieved with a Gilson Model 116 UV instrument operated at 230 nm (0.200 AUFS); flow rate: 1 mL/min; solvent program:

1:1 water–acetonitrile for 1 min, to 19:1 acetonitrile in 24 min, and hold at 19:1 acetonitrile for 8 min.

Preparative separations were performed with a Gilson Gradient Auto-Prep System and a preparative column (22.5 × 250 mm) of Spherex C-8 (10 μm), with a matching guard column; flow rate: 10 mL/min; solvent program: 4:1 acetonitrile-water, 0–21 min, to 19:1 acetonitrile–water in 4 min, and hold for 12 min. The fractions of interest were evaporated almost to dryness. The resulting pastes were suspended in water and freeze-dried to afford the resin-derived perbenzoates. Recoveries from the reverse-phase system were typically 50–80%.

Spectroscopy. — U.v. spectra of the perbenzoates in acetonitrile were recorded with a Shimadzu Model 265 spectrophotometer. F.-t. i.r. spectra (KBr pellets) were recorded with a Nicolet 5-DXB instrument. ^{1}H- and ^{13}C-n.m.r. spectra were recorded with a Bruker AM-400 (400 MHz) spectrometer. The hydroxyl protons of compounds **1** and **3** were completely exchanged with deuterium prior to the n.m.r. experiments, which were internally referenced to acetone-d_6 (^{1}H, 2.20 p.p.m.; ^{13}C, 29.8 p.p.m.). The spectra of compounds **2** and **4** were recorded for solutions in $CDCl_3$ or acetone-d_6, with tetramethylsilane (Me_4Si) as the internal reference. F.a.b.-m.s. was performed with a Kratos MS-50TC instrument, with matrix solutions of glycerol–water (for free D-glucosylureas) or dithiothreitol (DTT)–dithioerythritol (DTE) (for the perbenzoates). The DTT–DTE mixture is referred to as a "magic bullet" (m.b.).

N-*β*-D-*Glucopyranosylurea* (**1**). — D-Glucose (150 g), urea (150 g), and 0.5M sulfuric acid (75 mL) were treated as described by Benn and Jones[9]. A portion (30 g) of the resulting crystalline mono-D-glucosylurea–urea complex was placed in a Soxhlet apparatus and extracted with boiling methanol for 7 h, yielding 18.3 g of purified **1**. Crystallization from ethanol–water provided long needles of **1**, which were isolated by filtration and dried to constant weight at 60°. The yield was 15.1 g (14% overall), m.p. 207° (dec.) [lit.[9] 207° (dec.)], $[\alpha]_D^{20}$ −20.6° (*c* 2.0, water) (lit.[9] $[\alpha]_D^{20}$ −22°); F.-t.i.r.: 3470, 3369, 1682, 1567, 1089, and 1019 cm^{-1}; f.a.b.-m.s.: *m/z* (positive mode) 667 (3 M + H)$^+$, 445 (2 M + H)$^+$, 315 (M + glycerol + H)$^+$, and 223 (M + H)$^+$; (negative mode) 443 (2 M − H)$^-$, 313 (M + glycerol − H)$^-$, and 221 (M − H)$^-$.

Anal. Calc. for $C_7H_{14}N_2O_6$: C, 37.8; H, 6.4; N, 12.6. Found: C, 37.9; H, 6.2; N, 12.7.

N-*(2,3,4,6-Tetra-*O*-benzoyl-β-*D*-glucopyranosyl)urea* (**2**). — Anhydrous **1** (1.02 g) was suspended in freshly distilled pyridine (200 mL). Benzoic anhydride (20 g) and DMAP (8 g) were added, and the mixture was stirred overnight. The reaction was quenched with water (2 mL), and the mixture stirred for 15 min. Precipitation by pouring into cold water (1500 mL) afforded crude **2**, which could not be crystallized. The material was mixed with acetone (200 mL), the suspension filtered, and the compound reprecipitated with water (1000 mL); yield: 2.91 g (99%); m.p. 118° (lit.[5] 118–121°), $[\alpha]_D^{20}$ +33.8° (*c* 2.0, acetonitrile); F.-t.i.r.: 1732, 1269, 1109, 1095, 1070, 1027, and 710 cm^{-1}; u.v. (acetonitrile): λ in nm (ε in L/mol-

cm) 194 (145,500) and 229.5 (47,900); f.a.b.-m.s.: *m/z* (positive mode) 1278 (2 M + H)$^+$, 639 (M + H)$^+$, and 579 (M − urea + H)$^+$; (negative mode) 791 (M + mb)$^-$, 759 (M + BzOH − H)$^-$, 669 (M − BzOH + mb + H)$^-$, 637 (M − H)$^-$, and 517 (M − BzOH + H)$^-$.

Anal. Calc. for $C_{35}H_{30}N_2O_{10}$: C, 65.8; H, 4.7; N, 4.4. Found: C, 65.4; H, 5.0; N, 4.4.

N,N'-*Di-β*-D-*glucopyranosylurea* (**3**). — The preparation was conducted according to Benn and Jones[9]. Crystallization from ethanol–water provided **3** in 16% overall yield; m.p. 207° (dec.) [lit.[9] 345° (dec.)], $[\alpha]_D^{20}$ −32.8° (*c* 2.0, water) (lit.[9] $[\alpha]_D^{20}$ −34°); F.-t.i.r.: 3450–3330, 1644, 1585, 1074, and 1031 cm^{-1}; f.a.b.-m.s.: *m/z* (positive mode) 769 (2 M + H)$^+$, 477 (M + glycerol + H)$^+$, and 385 (M + H)$^+$; (negative mode) 383 (M − H)$^-$.

Anal. Calc. for $C_{13}H_{24}N_2O_{11}$: C, 40.6; H, 6.3; N, 7.3. Found: C, 40.3; H, 6.1; N, 7.4.

N,N'-*Bis(2,3,4,6-tetra*-O-*benzoyl-β*-D-*glucopyranosyl)urea* (**4**). — Compound **3** (550 mg) was suspended in freshly distilled pyridine (100 mL) to which were added benzoic anhydride (13.8 g) and DMAP (6.1 g). The mixture was stirred for 4 h and the reaction quenched with water (1 mL). Precipitation was effected by pouring into 800 mL of cold water. Filtration and subsequent drying afforded 1.52 g (88%) of crude **4**. Two recrystallizations from acetone–absolute ethanol provided small needles of **4**; m.p. 144–146° (lit.[10] 140–150°), $[\alpha]_D^{20}$ +12.9° (*c* 2.0, acetonitrile); F.-t.i.r.: 1732, 1272, 1108, 1095, 1070, 1027, and 709 cm^{-1}; u.v. (acetonitrile): λ in nm (ε in L/mol-cm) 193.6 (309,700) and 229.4 (102,000); f.a.b.-m.s.: *m/z* (positive mode) 1219 (M + 2 H)$^+$, 1218 (M + H)$^+$, 1095 (M − BzOH)$^+$, 973 (M − 2 BzOH)$^+$, and 579 (M − 2)$^+$; (negative mode) 1369 (M − mb − H)$^-$, 1337 (M + BzOH)$^-$, 1217 (M)$^-$, 1216 (M − H)$^-$, 1215 (M − 2 H)$^-$, and 1095 (M − BzOH)$^-$.

Anal. Calc. for $C_{69}H_{56}N_2O_{19}$: C, 68.1; H, 4.6; N, 2.3. Found: C, 67.6; H, 4.7; N, 2.3.

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