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PHASE-TRANSFER-CATALYZED D-GLUCOSYLATION: SYNTHESIS OF BENZOYLATED ARYL β-D-GLUCOPYRANOSIDES AND β-D-GLUCOPYRANOSYL-SUBSTITUTED CINNAMATES

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ABSTRACT

Phase-transfer-catalyzed D-glucosylation of chelated phenolic aglucons and substituted cinnamic acids, using 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide, resulted in the stereospecific formation of benzoylated aryl β-D-glucopyranosides and substituted-β-D-glucopyranosyl cinnamates, respectively, in good yields. The results conclusively disproved an earlier report that the phase-transfer method requires a nonparticipating group at C-2 or C-6 in the carbohydrate moiety. 1,2,3,4,6-Penta-*O*-benzoyl-β-D-glucopyranose was obtained as a minor side-product in all of these reactions. The possible mechanism of the phase-transfer method is discussed.

INTRODUCTION

Recently, glycosylation through phase-transfer catalysis has been drawing special attention owing to its good yields, mild reaction conditions, and high stereospecificity that could make it an ideal choice for the synthesis of complex, biologically active glycosides[1]. Whereas the merits of this method have been elaborately demonstrated in the nucleoside area[2–4], its application to the synthesis of glycosides[5–8], 1-thioglycosides[9–11], and *C*-glycosyl compounds[12] have been less explored.

Among the reports on *O*-glycosylation, the first described the condensation of resin-bound phenoxides with acetylated α-D-glycopyranosyl bromides to afford the acetylated aryl β-D-glycopyranosides, but had the limitation of initial preparation of resin-bound phenoxides[5]. Two reports that then followed made direct use of phenolic aglycons in a two-phase (organic–aq. alkali) system containing a phase-transfer catalyst, but they described contradictory results. Inch and co-workers[6] reported success in the reaction of benzylated α-D-glucopyranosyl bromide with phenolic aglycons to furnish benzylated aryl β-D-glucopyranosides, and failure on using acetylated α-D-glucopyranosyl bromide under similar conditions. This led

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these authors to decide that the phase-transfer procedure requires fully etherified D-glucopyranosyl derivatives or at least D-glucopyranosyl derivatives having non-participating groups at C-2 and C-6. However, these results were in contrast to the findings of Sidhu and co-workers[7], who achieved the successful reaction of several phenolic aglycons with acetylated α-D-glucopyranosyl bromide.

With this background, we undertook a systematic study aiming to resolve the controversy and to gain a deeper understanding of phase-transfer-catalyzed *O*-glycosylation. Our efforts have not only reinforced the findings of Sidhu and co-workers[7] but have extended the phase-transfer procedure to the synthesis of D-glucosyl esters as well. Our preliminary experiment related to the successful reaction of acetylated α-D-glucopyranosyl bromide with *p*-methoxycinnamic acid that culminated in the preparation of a synthetic analog of the natural product Kadalin[13] was reported earlier[8].

We now give a comprehensive account of phase-transfer-catalyzed D-glucosylation of chelated phenolic aglucons and cinnamic acids, using benzoylated D-glucosyl bromide. The chelated phenolic aglucons were chosen in order to test the efficacy of the phase-transfer D-glucosylation method. The choice of cinnamic acids, on the other hand, was dictated by the widespread occurrence of glycosyl esters of substituted cinnamic acids in Nature[14].

RESULTS AND DISCUSSION

The phenolic aglucons **2–5** reacted at room temperature with 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (**1**) in a dichloromethane–aq. sodium hydroxide, biphasic system employing cetyltrimethylammonium bromide as the phase-transfer catalyst, to afford an aryl β-D-glucoside tetrabenzoate (**6–9**) as the major product in each case.

The yield of, and physical data for, the new, crystalline products **6–9** are given in Table I. The observed ^{1}H-n.m.r. chemical shifts (δ 5.48–5.60) and coupling constants (*J* 8 Hz) of the anomeric proton of **6–9** were in accord with the β-D configuration.

Saponification of **6–9** with methanolic potassium carbonate[15] at 40° gave the free glucosides **12–15** in nearly quantitative yields. Table II lists their yields and

TABLE I

YIELDS OF AND PHYSICAL DATA FOR COMPOUNDS **6–9**

Compound	*Reaction period (h)*	*Yield (%)*	*M.p. (deg.)*	$[\alpha]_D^{20}$ *(deg.) (c 0.4, $CHCl_3$)*
6	24	45	134–135	+16.8
7	20	42	100–102	+30.9
8	18	46	152–153	+27.5
9	15	35	135–136	+63.3

TABLE II

YIELDS OF AND PHYSICAL DATA FOR COMPOUNDS **12–15**

Compound	*Yield (%)*	*M.p. (deg.)*		$[\alpha]_D$ *(deg.)*
		Found	*Lit.*	*Found* [*Lit.*]
12	90	143–144	142–143[a]	−61.3 (*c* 0.4, CH_3OH) [−66.7 (*c* 0.61, H_2O)[a]]
13	97	175–176	175[b]	−60.0 (*c* 0.4, CH_3OH) [−55.0 (*c* 1, C_2H_5OH)[b]]
14	92	154	154.5[c]	−56.8 (*c* 0.4, CH_3OH) [−60.4 (*c* 1.4, H_2O)[c]]
15	91	syrup	—	−69.5 (*c* 0.4, CH_3OH)

[a]Ref. 16. [b]Ref. 17. [c]Ref. 18.

physical data. Incidentally, the method provides a simple and easy laboratory preparation of the natural product helicin **14** (the Schiff base of which is an antitubercular agent and an erythrocyte-sickling inhibitor[19]) and of 2-carboxyphenyl β-D-glucoside (**12**), which is utilized for the study of enzyme action[16].

The success of the phase-transfer-catalyzed reaction of benzoylated α-D-glucosyl bromide (**2**) with phenolic aglucons led to extension of the method to the preparation of D-glucosyl esters. Thus, condensation at 60° of the substituted cinnamic acids **16–20** with **1** in 1,2-dichloroethane–aq. sodium hydroxide (biphasic system) with cetyltrimethylammonium bromide as the phase-transfer catalyst, resulted in formation of the desired D-glucosyl esters **21–25** as the major products. The yields and physical data of these new crystalline products are furnished in Table III. The assignment of the β-D configuration in **21–25** is based on the ^{1}H-n.m.r. chemical shifts (δ 6.24–6.28) and coupling constants (*J* 8 Hz) of the anomeric proton.

Attempted debenzoylation of **21–25**, even under relatively milder conditions, such as methanolic potassium carbonate[15] or ethanolic ammonia[20], did not afford the free D-glucosyl esters desired.

A careful investigation of the side products formed in the reaction, vital for understanding of the mechanism, was also made. The reaction of **1** with the phenolic aglucons **2–5**, as well as the substituted cinnamic acids **16–20** affords two side products, **10** and **11**, in each case. The identity of **10** as 1,5-anhydro-2,3,4,6-tetra-*O*-benzoyl-D-*arabino*-hex-1-enitol was established by comparing its physical and spectral data with those of an authentic sample prepared according to the procedure of Maurer and Petsch[21]. The identity of **11** was likewise unequivocally established as 1,2,3,4,6-penta-*O*-benzoyl-β-D-glucopyranose by comparing the physical and spectral data of **11** with those of an authentic sample prepared according to the procedure of Ness and co-workers[22].

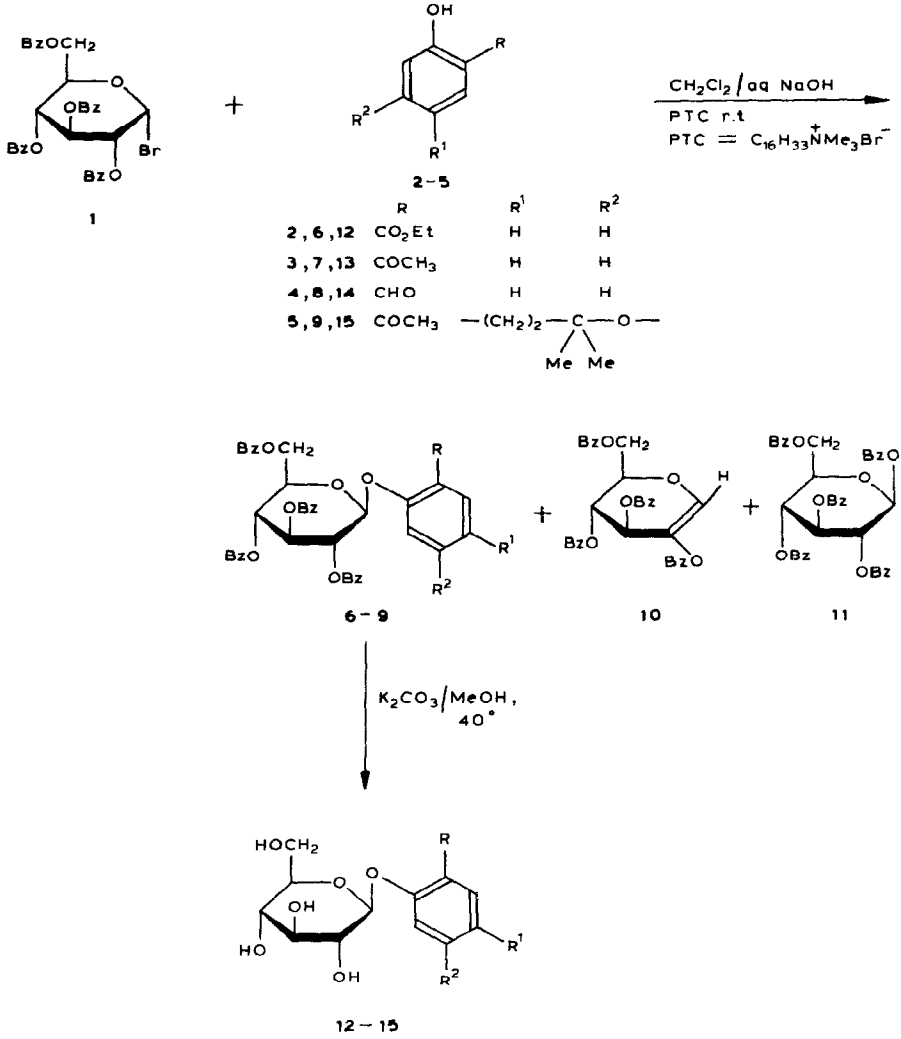
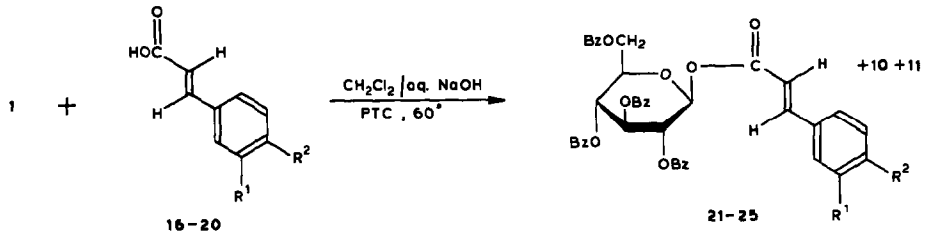


TABLE III

YIELDS OF AND PHYSICAL DATA FOR COMPOUNDS **21–25**

Compound	*Reaction period (h)*	*Yield (%)*	*M.p. (deg.)*	$[\alpha]_D^{20}$ *(deg.) (c 0.4, $CHCl_3$)*
21	3	82	185–186	−11.3
22	10	55	140–141	−23.0
23	12	68	150–151	−11.5
24	5	62	90	−21.3
25	8	53	171–172	−82.5



	16	17	18	19	20
	21	22	23	24	25
R^1	H	H	NO_2	OMe	H
R^2	H	Cl	H	OMe	NMe_2

Interestingly, use of benzoylated α-D-glucopyranosyl bromide (**1**) in the present phase-transfer-catalyzed reactions led to the formation of **10** (elimination product) and **11** as the side products, whereas, under similar conditions, acetylated α-D-glucopyranosyl bromide was reported[7] to give the corresponding elimination product and 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (hydrolysis product).

The formation of **11** in the reactions may be due to relative instability of benzoate *versus* acetate under alkaline phase-transfer conditions. The slow degradation of the benzoate from **1** under the alkaline phase-transfer conditions employed results in the formation of benzoate anion which, upon further reaction with **1**, leads to **11**.

With regard to the mechanism of phase-transfer-catalyzed D-glucosylation, it is reasonable to expect, by analogy with the observations made by Makosza[23] on two-phase, anion-transfer reactions, that the abstraction of a proton possibly takes place at the interface. The ion-pairs that are formed (either $Ar–CH=CH–CO_2^-N^+R_4$ $Ar\ O^-\ N^+R_4$) penetrate into the organic phase, where their reaction with bromide **1** in a relatively nonpolar medium (dichloromethane or 1,2-dichloroethane), being SN2 in nature, results in Walden inversion at the anomeric center.

The stereospecific formation of not only the major products **6–9** and **21–25** but also the side product **11**, as shown for the first time by the present work, lends credence to the foregoing explanation. Incidentally, after completion of our work[24], the phase-transfer catalyzed reaction of acetylated α-D-galactopyranosyl bromide with aryl aglycons was also shown to be successful[25].

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were measured with a 241 Perkin–Elmer automatic polarimeter. A magnetic stirrer was used throughout for thorough mixing of the biphasic reaction-media. U.v. spectra were recorded with a Varian Super-Scan-3 u.v.-visible spectrophotometer. I.r. spectra were recorded with a 257-B Perkin–Elmer grating spectrometer. ^{1}H-N.m.r. spectra were recorded with a Varian XL-100 spectrometer operated at 100 MHz,

using tetramethylsilane as the internal standard. Fast-atom-bombardment mass spectra were recorded with a Kratos MS-50 mass spectrometer.

Materials. — 2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl bromide[26] (**1**), cinnamic acids[27] **16–20**, and 6-acetyl-2,2-dimethyl-7-chromanol[28] (**5**) were prepared by well established procedures. Phenolic aglucons **2–5** were obtained commercially, and purified by distillation before use. Cetyltrimethylammonium bromide was purchased from E. Merck. Yields mentioned are of pure products isolated, and were not optimized.

Reaction of phenolic aglycons **2–5** *with 2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl bromide* (**1**): *General procedure.* — A solution of the aglycon (15 mmol) in dichloromethane (25 mL) was vigorously stirred at room temperature with 5% aqueous sodium hydroxide (25 mL, 30 mmol) and cetyltrimethylammonium bromide (0.91 g, 2.5 mmol). To this stirred mixture was added a solution of 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide (**1**; 10 mmol) in dichloromethane (25 mL), and stirring was continued for 15–30 h. The two phases were then separated. The organic layer was washed with 5% sodium hydroxide solution (2 × 10 mL) and several times with water, dried (sodium sulfate), filtered, and evaporated *in vacuo*. The aryl D-glucoside tetrabenzoates (**6–9**) were isolated in crystalline form by chromatography on a column of silica gel using 7:3 petroleum ether (b.p. 60–80°)–ethyl acetate, followed by crystallization from petroleum ether–ethyl acetate. Table I provides their yields and physical data.

*Ethyl 2-(2,3,4,6-tetra-*O*-benzoyl-β-*D*-glucopyranosyloxy)benzoate* (**6**). — U.v. ($CHCl_3$): 246 (4.24), 277 (3.73), 284 (3.69), and 298 (2.87) nm; i.r. (Nujol): 3070, 1735 (br), 1590, 1320, 1270 (br), 1070, 860, and 710 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 1.18 (t, 3 H, *J* 7 Hz, –O–CH_2–CH_3), 4.05 (q, 2 H, *J* 7 Hz, –O–CH_2–CH_3), 4.10–4.84 (m, 3 H, H-5′,H_R-6′,H_S-6′), 5.48 (d, 1 H, *J* 8 Hz, H-1′), 5.56–6.18 (m, 3 H, H-2,′3,′4), and 6.80–8.16 (m, 24 H, Ph).

Anal. Calc. for $C_{43}H_{36}O_{12}$: C, 69.35; H, 4.87. Found: C, 69.12; H, 4.72.

*2-(2,3,4,6-Tetra-*O*-benzoyl-β-*D*-glucopyranosyloxy)acetophenone* (**7**). — U.v. ($CHCl_3$): 247 (4.31), 277 (3.77), 284 (3.75), and 298 (3.43) nm; i.r. (Nujol): 3080, 1730 (br), 1680, 1590, 1320, 1270 (br), 1075, 845, 765, and 715 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 2.51 (s, 3 H, –COCH_3), 4.22–4.90 (m, 3 H, H-5′,H_R-6′,H_S-6′), 5.57 (d, 1 H, *J* 8 Hz, H-1′), 5.46–6.20 (m, 3 H, H-2′,3′,4′), and 6.84–8.12 (m, 24 H, Ph).

Anal. Calc. for $C_{42}H_{34}O_{11}$: C, 70.58; H, 4.79. Found: C, 70.73; H, 4.64.

*2-(2,3,4,6-Tetra-*O*-benzoyl-β-*D*-glucopyranosyloxy)benzaldehyde* (**8**). — U.v. ($CHCl_3$): 245 (4.45), 277 (3.72), 283 (3.69), and 306 (3.55) nm; i.r. (Nujol): 3070, 1730 (br), 1690, 1590, 1320, 1270 (br), 1070, 850, 760, and 715 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 4.18–4.88 (m, 3 H, H-5′,H_R-6′,H_S-6′), 5.52 (d, 1 H, *J* 8 Hz, H-1′), 5.40–6.20 (m, 3 H, H-2′,3′,4′), 6.80–8.32 (m, 24 H, Ph), and 10.30 (s, 1 H, –C*H*O).

Anal. Calc. for $C_{41}H_{32}O_{11}$: C, 70.28; H, 4.60. Found: C, 70.45; H, 4.40.

*6-Acetyl-2,2-dimethyl-7-(2,3,4,6-tetra-*O*-benzoyl-β-*D*-glucopyranosyloxy)-chroman* (**9**). — U.v. ($CHCl_3$): 244 (4.48), 273 (4.20), and 302 (3.90) nm; i.r.

(Nujol): 3060, 1740, 1730 (br), 1670, 1580, 1320, 1270 (br), 1095, 840, and 710 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 1.28 and 1.30 (s, 3 H each, *gem*-dimethyl), 1.76 (t, 2 H, *J* 7 Hz, CH_2-3), 2.52 (s, 3 H, –COCH_3), 2.70 (t, 2 H, *J* 7 Hz, CH_2-4), 4.20–4.88 (m, 3 H, H-5′,H_R-6′,H_S-6′), 5.60 (d, 1 H, *J* 8 Hz, H-1′), 5.48–6.16 (m, 3 H, H-2′,3′,4′), 6.54 (s, 1 H, H-8), and 7.14–8.20 (m, 21 H, Ph).

Anal. Calc. for $C_{47}H_{42}O_{12}$: C, 70.67; H, 5.30. Found: C, 70.79; H, 5.58.

Debenzoylation of compounds **6–9**: *General procedure.* — A suspension of the compound (1 mmol) in methanolic potassium carbonate (50 mL, containing 48.5 mL of methanol and 1.5 mL, of water saturated with potassium carbonate) was vigorously stirred for 5–10 min at 40°, resulting in a clear solution which was cooled, diluted with methanol to 200 mL, and passed through a column of IR-120 cation-exchange resin. The eluate was evaporated to dryness *in vacuo*. Chromatography of the crude syrup on silica gel with 9:1 ethyl acetate–methanol, followed by crystallization from ethanol, afforded the free glycosides **12–15**. Table II lists their yields and physical data.

*6-Acetyl-7-(β-*D*-glucopyranosyloxy)-2,2-dimethylchroman* (**15**). — I.r. (Nujol): 3400 (br), 1670, 1580, 1300, 1270, 1070 (br), 1020, and 890 cm^{-1}; ^{1}H-n.m.r. (Me_2SO-d_6): δ 1.30 (s, 6 H, *gem*-dimethyl), 1.78 (t, 2 H, *J* 7 Hz, CH_2-3), 2.58 (s, 3 H, –COCH_3), 2.70 (t, 2 H, *J* 7 Hz, CH_2-4), 3.00–3.90 and 4.40–5.40 (m, protons of D-glucosyl group), 6.58 (s, 1 H, H-8), and 7.50 (s, 1 H, H-5).

Reaction of cinnamic acids (**16–20**) *with 2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl bromide* (**1**): *General procedure.* — A solution of the aglucon (12 mmol) in 1,2-dichloroethane (25 mL) was stirred vigorously at 60° with 5% aqueous sodium hydroxide (25 mL, 30 mmol) and cetyltrimethylammonium bromide (0.91 g, 2.5 mmol). To this stirred mixture was added a solution of **1** (6.60 g, 10 mmol) in 1,2-dichloroethane (25 mL), and stirring was continued for 3–12 h. The mixture was then cooled and worked-up as before. Column chromatography of the crude product on silica gel with 4:1 petroleum ether (60–80°)–ethyl acetate, followed by crystallization from ethyl acetate–petroleum ether, furnished **21–25** in crystalline form. Table III describes their yields and physical data.

*2,3,4,6-Tetra-*O*-benzoyl-1-*O*-cinnamoyl-β-*D*-glucopyranose* (**21**). — U.v. ($CHCl_3$): 246 (4.28), 278 (4.40), and 284 (4.42); i.r. (Nujol): 3070, 1740, 1730, 1640, 1590, 1320, 1270, 1070, 855, 775, and 715 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 4.16–4.80 (m, 3 H, H-5,H_R-6,H_S-6), 5.64–6.20 (m, 3 H, H-2,3,4), 6.27 (d, 1 H, *J* 8 Hz, H-1), 6.42 (d, 1 H, *J* 16 Hz, *trans*–CH=CH–), and 7.12–8.24 (m, 26 H, Ar–H and *trans* –CH=CH–).

Anal. Calc. for $C_{43}H_{34}O_{11}$: C, 71.06; H, 4.71. Found: C, 71.54; H, 4.45.

*2,3,4,6-Tetra-*O*-benzoyl-1-*O*-(4-chlorocinnamoyl)-β-*D*-glucopyranose* (**22**). — U.v. ($CHCl_3$): 246 (4.35), 280 (4.40), 286 (4.41), and 296 (4.36) nm; i.r. (Nujol): 3070, 1725 (br), 1630, 1590, 1315, 1260 (br), 1070, 855, 825, and 710 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 4.20–4.80 (m, 3 H, H-5,H_R-6,H_S-6), 5.60–6.15 (m, 3 H, H-2,3,4), 6.24 (d, 1 H, *J* 8 Hz, H-1), 6.34 and 7.68 (d, 1 H each, *J* 16 Hz, *trans* –CH=CH–), and 7.20–8.20 (m, 24 H, Ph).

Anal. Calc. for $C_{43}H_{33}ClO_{11}$: C, 67.85; H, 4.37. Found: C, 68.48; H, 4.62.

2,3,4,6-Tetra-O-benzoyl-1-O-(3-nitrocinnamoyl)-β-D-glucopyranose (**23**). — U.v. ($CHCl_3$): 246 (4.57) and 268 (4.57) nm; i.r. (Nujol): 3060, 1730 (br), 1645, 1310, 1270 (br), 1070, 810, and 710 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 4.22–4.90 (m, 3 H, H-5,H_R-6,H_S-6), 5.58–6.20 (m, 3 H, H-2,3,4), 6.28 (d, 1 H, *J* 8 Hz, H-1), 6.50 (d, 1 H, *J* 16 Hz, *trans* –CH=CH–), and 7.02–8.40 (m, 25 H, Ph and *trans* –CH=CH–).

Anal. Calc. for $C_{43}H_{33}NO_{13}$: C, 66.92; H, 4.31; N, 1.82. Found: C, 66.85; H, 4.14; N, 1.68.

2,3,4,6-Tetra-O-benzoyl-1-O-(3,4-dimethoxycinnamoyl)-β-D-glucopyranose (**24**). — U.v. ($CHCl_3$): 247 (4.37), 280 (4.01), 287 (4.06), 303 (4.08), and 333 (4.37); i.r. (Nujol): 3060, 1730 (br), 1630, 1585, 1320, 1265 (br), 1070, 850, 810, and 710 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 3.92 (s, 6 H, 2 $-OCH_3$), 4.00–4.78 (m, 3 H, H-5,H_R-6,H_S-6), 5.60–6.18 (m, 3 H, H-2,3,4), 6.24 (d, 1 H, *J* 8 Hz, H-1), 6.25 and 7.68 (d, 1 H each, *J* 16 Hz, *trans* –CH=CH–), 6.84 (d, 1 H, *J* 9 Hz, H-5′), 7.08 (dd, 1 H, *J* 9, 2 Hz, H-6′), and 7.16–8.10 (m, 21 H, Ph).

Anal. Calc. for $C_{45}H_{38}O_{13}$: C, 68.70; H, 4.87. Found: C, 68.39; H, 4.83.

2,3,4,6-Tetra-O-benzoyl-1-O-(4-dimethylaminocinnamoyl)-β-D-glucopyranose (**25**). — U.v. ($CHCl_3$): 245 (4.45), 283 (3.61), 326 (3.81), and 381 (4.48) nm; i.r. (Nujol): 3065, 1740, 1730, 1630, 1315, 1270, 1095, 820, and 715 cm^{-1}; ^{1}H-n.m.r. ($CDCl_3$): δ 3.02 [s, 6 H, $-N(CH_3)_2$], 4.20–4.90 (m, 3 H, H-5,H_R-6,H_S-6), 5.60–6.15 (m, 3 H, H-2,3,4), 6.14 and 7.66 (d, 1 H each, *J* 16 Hz, *trans* –CH=CH–), 6.24 (d, 1 H, *J* 8 Hz, H-1), 6.62 (d, 2 H, *J* 9 Hz, H-3′,5′), and 7.14–8.10 (m, 22 H, Ph).

Anal. Calc. for $C_{45}H_{39}NO_{11}$: C, 70.21; H, 5.10; N, 1.82. Found: C, 70.03; H, 5.36; N, 1.92.

1,5-Anhydro-2,3,4,6-tetra-O-benzoyl-D-arabino-*hex-1-enitol* (**10**). — Column chromatography of the crude product obtained in each of the reactions of **2**–**5**, as well as of **16**–**20**, with **1** on silica gel with 9:1 petroleum ether (60–80°)–ethyl acetate, followed by crystallization from petroleum ether–ethyl acetate, furnished **10**. The yield of **10** varied from 15 to 25% in the first set of reactions, and from 10 to 20% in the second; m.p. 123°, $[\alpha]_D^{20}$ −81° (*c* 0.4, $CHCl_3$); lit.[21] m.p. 123°, $[\alpha]_D^{20}$ −77° (*c* 2, $CHCl_3$).

1,2,3,4,6-Penta-O-benzoyl-β-D-glucopyranose (**11**). — Column chromatography of the crude product, obtained in each of the reactions of **2**–**5**, as well as of **16**–**20**, with **1**, on silica gel with 17:3 petroleum ether (60–80°)–ethyl acetate, followed by crystallization from petroleum ether–ethyl acetate, afforded **11**. Its yield varied from 10–15% in the first set of reactions and 5–10% in the second; m.p. 157–158°, $[\alpha]_D^{20}$ +20.5° (*c* 0.4, $CHCl_3$); lit.[22] 189–192° (crystallized from aqueous acetone), $[\alpha]_D$ +24.2° (*c* 2.6, $CHCl_3$). Recrystallization of **11** from aqueous acetone gave a sample which, after drying at 150°, melted at 189–192°. F.a.b.-mass spectrum: ($\overset{+}{N}H_4$ + $\overset{+}{N}a$ + 1-thioglycerol) *m/z* 1423 (10%), 1279 (14), 723 (25), 579 (70), 451 (7), 237 (32), 217 (50), 131 (93), and 105 (100).

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