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C-GLUCOSYLARENES FROM *O*-α-D-GLUCOSYL TRICHLOROACETIMIDATES. STRUCTURE OF BERGENIN DERIVATIVES*

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ABSTRACT

C-Glucosylation of oxysubstituted benzene derivatives with *O*-α-D-glucopyranosyl trichloroacetimidate gave mainly β-D-glucopyranosylarenes. The most efficient catalysts were diethyl ether·boron trifluoride, diethyl ether·zinc chloride, and zinc chloride. The reaction was successful with fully and partially *O*-protected phloroglucinols and it was also compatible with an additional *C*-alkyl substituent. Introduction of an electron-withdrawing, *C*-acetyl substituent into the phloroglucinol structure lowered the reactivity. The reaction could be extended to 1,2,3- and 1,2,4-trioxysubstituted benzene derivatives to give the bergenin derivative (3*R*,4*R*,4a*R*,10b*S*)-3,4-diacetoxy-2-acetoxymethyltetrahydropyrano[5,6-*C*]-3,4-dihydroisocoumarin *via* an intramolecular version of this reaction. O-Protected resorcinols and *C*-substituted derivatives of dioxysubstituted benzenes gave various 4-*C*-glucosyl-benzene and chroman derivatives. An anomeric mixture of *C*-glucosyl derivative of anthrone was obtained from 9-trimethylsilyloxyanthracene (as a monoxysubstituted benzene derivative). The pure β-D anomer was synthesized from the *O*-acylated trichloroacetimidate.

INTRODUCTION

C-Glycosylarenes, and amongst these especially *C*-glucosylarenes, are widespread in Nature and they have been isolated from very different sources[1]. They are of interest as natural dye-stuffs (vitexin[2], carminic acid[2]) and as compounds having interesting physiological properties (*C*-glycosyltetrahydrocannabinol[3], hedamycin[4], kyanamycin[4], bergenin[5–7], etc.). Improved antitumor activity is expected from *C*-glycosylanthracyclinones due to differences in their metabolism[8]. Most of the compounds mentioned are derivatives of oxysubstituted benzenes and benzoquinones, for which an interesting hypothesis for antitumor activity has been proposed[9].

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O-Glycopyranosyl trichloroacetimidates have proven to be excellent glycosyl donors with silylenol ethers as *C*-acceptors[10]. Therefore, oxy-substituted benzene derivatives would be substrates in this Friedel–Crafts type reaction as well[11]. Earlier Friedel–Crafts type reactions with glycopyranosyl halides gave frequently both anomers and unsatisfactory results because of low reactivity[12]. Considerably lower reactivity has been observed for pyranoses as compared to furanoses[13].

RESULTS AND DISCUSSION

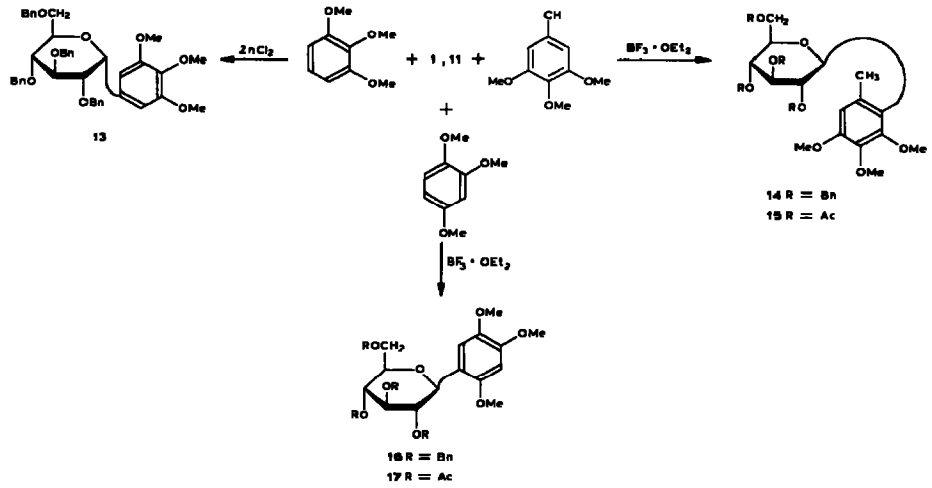
Our preliminary investigations[11] with *O*-α-D-glucopyranosyl trichloroacetimidate (**1**), phloroglucinol trimethyl ether, and diethyl ether·boron trifluoride as catalyst gave excellent yields of the β-D-glucosyl compound **2**, making the yield of this method competitive with those of any other reported methods[12–14]. In the meantime also, the *O*-β-D-glucopyranosyl imidate **11** could be successfully used[15] for the synthesis of compound **2**. Therefore, we undertook a more detailed investigation[15] of the scope of this *C*-glucosyl-bond-forming reaction with the glucosyl donor **1**.

Electron-rich benzene derivatives are labile to acid treatment; therefore, the selection of the catalyst system was crucial for these reactions. A thorough investigation of various Lewis-acid catalysts revealed that, besides the efficient diethyl ether·borontrifluoride catalyst*, the weak Lewis-acids, diethyl ether·zinc chloride and zinc chloride itself, are the most efficient catalysts. This result was clearly demonstrated with phloroglucinol tribenzyl ether and imidate **1**, which yielded, with diethyl ether·zinc chloride as catalyst, clearly the corresponding β-*C*-glucosyl compound **3** as main product, in addition to some α-D anomer (89%; ratio of β to α, 3:1). Diethyl ether·borontrifluoride led mainly to the decomposition of the glucosyl acceptor[14].

Investigations of various substituted phloroglucinol derivatives gave interesting results. With the dimethyltrimethylsilyl ether of phloroglucinol and diethyl ether·borontrifluoride, only the regioisomer **4** could be isolated. However, the dimethyl-*O*-(1,1-dimethylethyl)diphenylsilyl ether afforded, under the same conditions, preponderantly the regioisomer **5** (62%; ratio of **5** to **4** 3:1). For structural assignments, **4** was debenzylated and subsequently *O*-acetylated to give **6**. Compounds **2–5** are suitable starting materials for *C*-glucosylflavone syntheses. This is even more so for the *C*-glucosyl compound **7**, which was obtained from methyl 2,4,6-trimethoxyphenylpropionate in high yield. It was transformed into the *O*-acetyl derivative **8**. 2-Isopropenylphloroglucinol trimethyl ether gave with diethyl ether·zinc chloride as catalyst, the regioisomers **9** and **12** owing to electrophilic attack at the benzene nucleus or at the electron-rich side chain, followed by prototropy. Introduction of an electron withdrawing substituent into the phloroglucinol residue led to lowered reactivity; for instance, 2-acetylphloroglucinol dimethyl

*This catalyst system[16] was mainly used for *O*-glycosyl trichloroacetimidate activation.

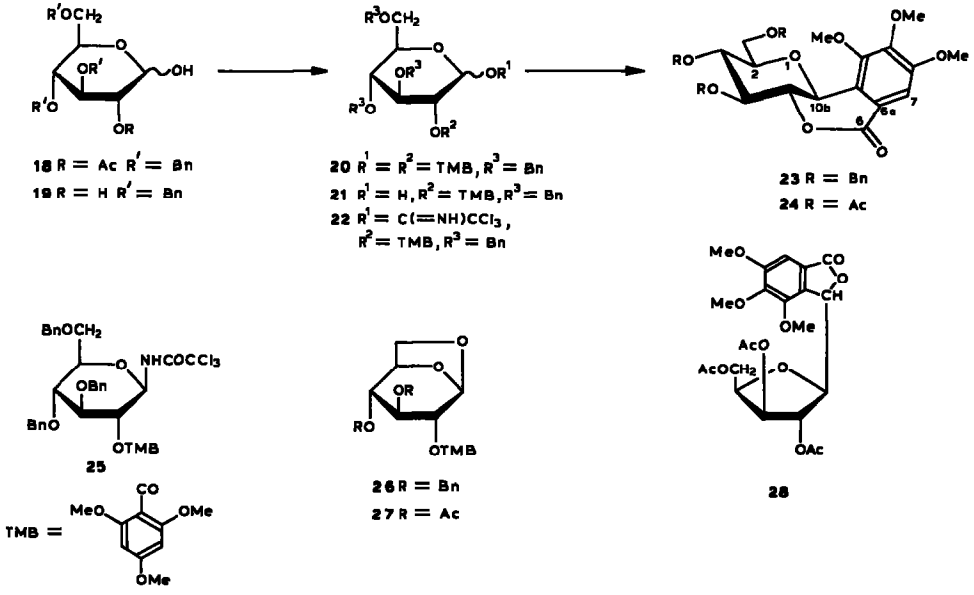
2 R¹ = R² = R⁴ = Me, R³ = H, R⁵ = Bn
3 R¹ = R² = R⁴ = R⁵ = Bn, R³ = H
4 R¹ = R² = Me, R³ = R⁴ = H, R⁵ = Bn
5 R¹ = R⁴ = Me, R² = R³ = H, R⁵ = Bn
6 R¹ = R² = Me, R³ = H, R⁴ = R⁵ = Ac
7 R¹ = R² = R⁴ = Me, R³ = (CH2)2CO2Me, R⁵ = Bn
8 R¹ = R² = R⁴ = Me, R³ = (CH2)2CO2Me, R⁵ = Ac
9 R¹ = R² = R⁴ = Me, R³ = C(CH3)=CH2, R⁵ = Bn
10 R¹ = R² = Me, R³ = COMe, R⁴ = H, R⁵ = Bn
1
11
12



ether afforded the *C*-glucosyl compound **10** only in a modest yield.

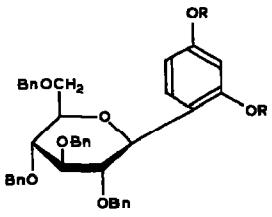
The result obtained for compound **10** lowered our expectations for the regioisomeric trimethoxy-substituted benzene derivatives, since one of the methoxy groups would inductively deactivate the benzene nucleus for electrophilic attack. This was also observed with pyrogallol trimethyl ether; only the α-D isomer **13** was obtained in low yield. However, treatment of the 5-methyl-substituted derivative with imidate **11** exhibited a very different behavior; the β-D isomer **14** was isolated again in fairly good yield (47%); only traces (3%) of the corresponding α-D isomer could be isolated. Also, 1,2,4-trimethoxybenzene gave the *C*-β-D-glucosyl compound **16** from **1** in reasonable yield. For structural assignments, compounds **14** and **16** were transformed into the *O*-acetyl derivatives **15** and **17**, respectively.

The results obtained for compound **14** were quite promising for a short synthesis of the *O*-acylated bergenin dimethyl ether[6,7] **24** *via* an intramolecular *C*-glucosyl-bond formation. Bergenin-type compounds have been isolated from a heartwood extraction of *Macaranga peltata*, a small tree commonly found in Indian forests. A gum powder of this tree has been used in Indian medicine for the treatment of veneral diseases[7]. In our approach, the D-glucose derivative **18** was synthesized from the easily available 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-D-glucose[17], and deacetylation gave **19**. Treatment with 3,4,5-trimethoxybenzoyl chloride in the presence of methylpyridine in toluene afforded the 1,2-digalloyl-D-glucose derivative **20**, which was selectively transformed into the 2-galloyl derivative **21** by treatment with hydrazine acetate. The α and β mixture of trichloroacetimidates **22** was obtained with trichloroacetonitrile–potassium carbonate and subsequent addition of sodium hydride in almost quantitative yield (98%; ratio of α to β, 6:1); potassium carbonate alone gave a 2:1 ratio of the anomers.

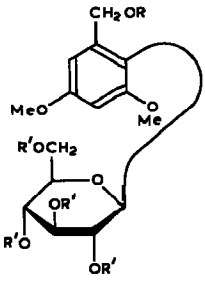


Several methods were investigated for the intramolecular ring-closure of the trichloroacetimidates **22**. For instance, treatment of the α-D anomer of **22** with trifluoromethanesulfonic acid as catalyst gave, *via* imidate rearrangement, the glucosylamine derivative **25** in good yield. Other strong Lewis acids led to the formation of some additional 1,6-anhydro-D-glucose derivative **26**, which was also obtained from the β-D anomer of **22** with diethyl ether·zinc chloride as catalyst; the main product in the latter reaction was compound **21**. Borontrifluoride treatment of the α-D anomer of trichloroacetimidate **22** in toluene afforded, in addition to some 1,6-anhydro-D-glucose derivative **26**, a new compound **23**, which after hydrogenolytic debenzylation and *O*-acetylation had ^{1}H-n.m.r. spectral data in agreement with structure **24** proposed for bergenin dimethyl ether[6,7]. All the sugar ring protons could be fully assigned by the use of different solvents. Their chemical shifts and coupling constants are in accordance with expectations, $J_{1',2'}$ 7.8, $J_{2',3'}$ 9.5, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.5, $J_{5',6'}$ 5.2, and $J_{5',6''}$ 2.5 Hz; however, these data are not in agreement with the published data for the natural product[7]. In our opinion, the ^{1}H-n.m.r. and mass spectral data published for the natural product rather suggest structure **28**; however, further work is required for the final structural elucidation of this compound.

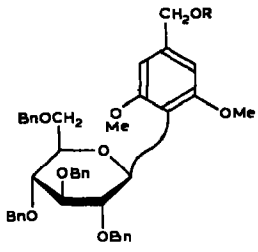
Various 1,3-dioxybenzenes could be successfully *C*-glucosylated with the trichloroacetimidate **1**. Resorcinol dimethyl ether and resorcinol bis(trimethylsilyl) ether gave the *C*-glucosyl components **29** and **30**, respectively, in high yield. [(1,1-Dimethyl)ethyl](diphenyl)silyloxymethyl resorcinal dimethyl ether afforded a 2:1 mixture of the regioisomers **31** and **34**, which were immediately desilylated with tetrabutylammonium fluoride and isolated as compounds **32** and **35** in good yield.



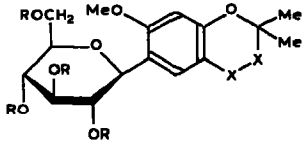
29 R = Bn, R^1 = Me
30 R = Bn, R^1 = H



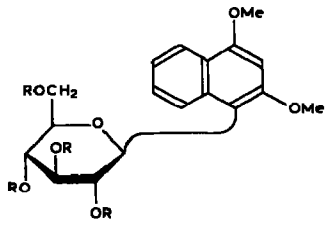
31 R = Bu^tPh_2Si, R' = Bn
32 R = H, R' = Bn
33 R = R' = Ac



34 R = Bu^tMe_2Si
35 R = H

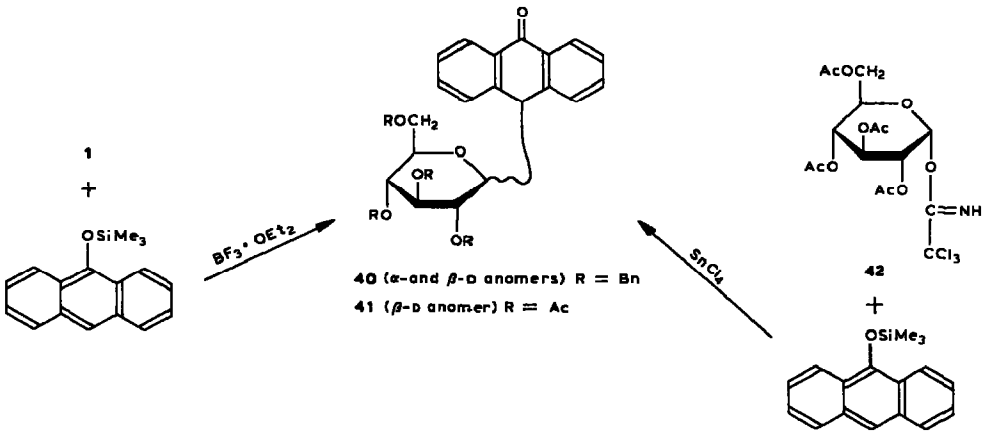


36 R = Bn, X-X = CH=CH
37 R = Ac, X-X = CH_2—CH_2



38 (Rotamers) (a and b), R = Bn
39 R = Ac

Compound 32 was also transformed into the *O*-acetyl derivative 33. The occurrence of the oxysubstituted chromene and naphthalene nuclei in natural *C*-glucosyl compounds led us to investigate the *C*-glucosylation of 7-methoxy-2,2-dimethyl-2*H*-chromene and 1,3-dimethoxynaphthalene as 1,3-dialkoxybenzene derivatives. Thus, the *C*-glucosyl compounds 36 and 38 were obtained and, after hydrogenolytic debenzylation and *O*-acetylation, the *C*-glucosyl compounds 37 and 39. Restricted rotation around the *C*-glucosyl bond was observed in ^{1}H-n.m.r. measurements, for instance for compounds 6, 7, 8, 33, and 39. A clear separation of the two 1,2-rotamers was possible with the *C*-glucosylnaphthalene 38.



40 (α- and β-D anomers) R = Bn
41 (β-D anomer) R = Ac
42

Simple monoalkoxy-benzenes were not reactive enough for this *C*-glucosyl-bond-forming reaction. However, 9-trimethylsilyloxyanthracene gave a mixture of the anomers of the *C*-glucosylanthrone **40** which could not be separated. The pure *C*-β-D-glucosyl compound **41** was obtained with the *O*-acetylated *O*-α-D-glucopyranosyl trichloroacetimidate **42**.

The structures of the new compounds (anomeric configuration and regioisomeric constitution) were assigned by ^{1}H- and ^{13}C-n.m.r. data. Off-resonance spectra and spectra recorded at high temperature were obtained, some compounds being converted into *O*-acetyl derivatives (**6**, **8**, **15**, **17**, **24**, **33**, **37**, and **39**). The *O*-benzyl compounds **32** and **38** (rotamers) seem to have a twisted conformation according to the coupling constants; this may be due to steric strain around the glycosidic bond. For compound **41**, the ^{1}H-n.m.r. spectral assignments reported[18] could not be verified. The observed preferential formation of *C*-β-D-glucopyranosyl compounds from trichloroacetimidate **1**, contrary to the findings with silylenol ethers as acceptors[10], could be due to a lower steric strain in the β-transition state for the sterically-demanding acceptors used in the present study. This view is supported by the exclusive isolation of the *C*-α-D-glucopyranosyl derivative **13** with the less-hindered pyrogallol trimethyl ether.

EXPERIMENTAL

General. — Melting points are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter. ^{1}H-N.m.r. and ^{13}C-n.m.r. spectra were recorded, for solution in the solvents noted (Me_4Si, 0.00 δ), with Bruker WP 80 CW, Bruker WM 250 Cryospec, and Jeol FX 90 Q instruments. R_F values refer to t.l.c. performed on silica gel (Merck) with the solvent systems noted. Column chromatography was performed under normal pressure with silica gel (Merck, 70–230 mesh ASTM and 230–400 mesh ASTM for flash chromatography) and under elevated pressure with silica gel (Merck, "LiChroprep" Si 60, 40–60 μm) with the solvent systems noted (petroleum ether, 40–70°).

The following starting materials were commercially available and purchased from Aldrich Co.: 1,3,5-Trimethoxybenzene, 3,4,5-trimethoxytoluene, 1,2,4-trimethoxybenzene, 1,3-dimethoxybenzene, precocene I (2,2-dimethyl-7-methoxy-2*H*-chromene), and 1,3-dimethoxynaphthalene.

*2,4,6-Trimethoxy-1-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)benzene*[11] (**2**). — (*a*) *From* O-*(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl) trichloroacetimidate*[19] (**1**). A solution of **1** (2.06 g, 3 mmol) and 1,3,5-trimethoxybenzene (0.50 g, 3 mmol) in dichloromethane (20 mL) was treated with 0.5M diethyl ether·BF_3 solution in anhydrous dichloromethane (6 mL, 3 mmol) at room temperature. After 3 h, excess saturated solution of $NaHCO_3$ in water was added. The organic layer was separated, dried (Na_2SO_4), and evaporated. The oily residue was purified on silica gel by flash chromatography (4:1, v/v, petroleum ether–ethyl acetate); yield 1.55 g (76%), colorless oil, $[\alpha]_{578}^{20}$ +5.4° (*c* 1.0, chloroform); R_F (4:1, v/v, petroleum

ether–ethyl acetate) 0.35. The physical data have been confirmed independently[13].

Anal. Calc. for $C_{43}H_{46}O_8$ (690.8): C, 74.75; H, 6.71. Found: C, 74.36; H, 6.72.

(*b*) *From* O-*(2,3,4,6-tetra-*O-*benzyl-β-*D-*glucopyranosyl)* N,*2,2-tri-(4-chlorophenyl)acetimidate*[20] (**11**). A solution of **11** (1.05 g, 1.15 mmol) and 1,3,5-trimethoxybenzene (0.33 g, 1.96 mmol) in anhydrous dichloromethane (10 mL) was treated with 0.1M diethyl ether·BF_3 solution in dichloromethane (2 mL, 0.2 mmol) at room temperature. After 20 min, the reaction mixture was worked-up, as described above, to yield **2** (0.53 g, 67%) having identical physical data.

*2,4,6-Tribenzyloxy-1-(2,3,4,6-tetra-*O-*benzyl-β-* (**3**) *and -α-*D-*glucopyranosyl)benzene.* — (*a*) *Synthesis of 1,3,5-tribenzyloxybenzene.* To a solution of 1,3,5-trihydroxybenzene (3.96 g, 24.4 mmol) in anhydrous *N,N*-dimethylformamide (50 mL) was added NaH (2.50 g, 104.2 mmol) under N_2 at −20° and, after 1 h, benzyl bromide (14.08 g, 82.3 mmol). The mixture was kept for 2 h at −20°, then methanol was added to eliminate the excess of NaH, and the suspension was treated with water (100 mL). The organic material was extracted with dichloromethane (3 × 70 mL) and the organic phase dried ($MgSO_4$) and evaporated. The solid residue crystallized from ethanol–water to yield 7.32 g (76%), m.p. 89°; lit.[21] m.p. 39–41° (acetic acid); ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 7.48–7.15 (m, 15 H, 3 C_6H_5), 6.63 (s, 3 H, H-2,4,6), and 5.01 (s, 6 H, 3 CH_2).

Anal. Calc. for $C_{27}H_{24}O_3$ (396.5): C, 81.79; H, 6.10. Found: C, 81.86; H, 6.11.

(*b*) *Synthesis of a mixture of* **3** *and its α-*D *anomer.* As described for the preparation of **2**, procedure (*a*) was applied to a solution, in anhydrous dichloromethane (15 mL) of **1** (0.95 g, 1.38 mmol), 1,3,5-tribenzyloxybenzene (0.55 g, 1.38 mmol), and 0.56M diethyl ether·zinc chloride in anhydrous dichloromethane (10 mL, 5.60 mmol) to give, after 1 h, an oily residue that was purified on silica gel by flash chromatography (4:1, v/v, petroleum ether–ethyl acetate), yield 1.13 g (88%; ratio of β- to α-D anomer, 3:1), colorless oil; R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.54; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.51–6.91 (m, 35 H, 7 C_6H_5), 6.25, 6.24 (2 s, 2 H, H-4,6), 5.99 (dd, 0.25, H, $J_{1',2'}$ 6.1 Hz, H-1′,α), and 5.19–3.44 (m, 20.75 H).

Anal. Calc. for $C_{61}H_{58}O_8$ (919.1): C, 79.71; H, 6.36. Found: C, 79.63; H, 6.48.

*3,5-Dimethoxy-2-(2,3,4,6-tetra-*O-*benzyl-β-*D-*glucopyranosyl)phenol* (**24**) *and 3,5-dimethoxy-4-(2,3,4,6-tetra-*O-*benzyl-β-*D-*glucopyranosyl)phenol* (**5**). — (*a*) *Synthesis of 3,5-dimethoxy-1-trimethylsilyloxybenzene.* 3,5-Dimethoxyphenol (1.00 g, 6.49 mmol) was refluxed in hexamethyldisilazane (5 mL) and chlorotrimethylsilane (5 mL) for 12 h. Distillation gave a colorless liquid (1.38 g, 94%), b.p. 72° (25 Pa); ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 6.28–6.15 (m, 3 H, C_6H_3), 3.80 (s, 6 H, 20 Me), and 0.25 (s, 9 H, 3 SiMe).

Anal. Calc. for $C_{11}H_{18}O_3Si$ (226.3): C, 58.37; H, 8.02. Found: C, 58.35; H, 7.75.

(*b*) *Synthesis of (1,1-dimethylethyl)diphenylsilyloxy-3,5-dimethoxybenzene.*

This compound was synthesized from dimethoxyphenol and chloro(1,1-dimethylethyl)diphenylsilane according to a published general procedure[22], yield 53%, R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.78; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 8.05–7.50 (m, 10 H, 2 C_6H_5), 6.00 (c.m., 3 H, H-2,4,6), 3.63 (s, 6 H, 2 OMe), and 1.10 (s, 9 H, CMe_3): m.s.: *m/e* 392 (M^+), 199 (100%).

(*c*) *Synthesis of* **4**. As described for the preparation of **2**, procedure (*a*) was applied to **1** (0.93 g, 1.35 mmol), 3,5-dimethoxytrimethylsilyloxybenzene (0.35 g, 1.55 mmol) in anhydrous dichloromethane (5 mL), and 0.25M diethyl ether·BF_3 in dichloromethane (4 mL, 1.00 mmol) to give, after 1 h, an oily residue that was purified on silica gel by flash chromatography (7:3, v/v, petroleum ether–ethyl acetate), yield 0.30 g (33%), colorless oil, $[\alpha]_{578}^{23}$ +33° (*c* 1, chloroform), R_F (4:1, v/v, toluene–ethyul acetate), 0.35; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.98 (s, 1 H, OH), 7.24–6.91 (m, 20 H, 4 C_6H_5), 6.07, 5.98 (2 d, 2 H, $J_{4,6}$ 1.3 Hz, H-4,6), 4.96–3.51 (m, 15 H, 4 CH_2, 7 sugar H), 3.68, and 3.59 (2 s, 6 H, 2 OMe); ^{13}C-n.m.r. (62.97 MHz, $CDCl_3$): δ 161.4, 158.6, 158.2 (3 s, 3 C, C-1,3,5), 138.8, 138.2, 138.0, 137.9 (4 s, 4 [C-1 (C_6 H_5)], 128.3–127.4 (C_6H_5), 104.9 (s, 1 C, C-2), 94.9, 91.4 (d, 2 C, C-4,6), 86.1, 81.6, 78.6, 75.5, 75.1, 75.0, 74.5, 73.4, 68.1)4 C_6H_5-CH_2, 6 sugar C), 55.6, and 55.2 (2 q, 2 C, 2 OCH_3).

Anal. Calc. for $C_{42}H_{44}O_8$ (676.8): C, 74.54; H, 6.55. Found: C, 74.28; H, 6.78.

(*d*) *Synthesis of* **5**. As described for the preparation of **2**, procedure (*a*) was applied to **1** (0.68 g, 1.01 mmol), (1,1-dimethylethyl)diphenylsilyloxy-3,5-dimethoxybenzene (0.68 g, 1.73 mmol) in anhydrous dichloromethane (15 mL), and 0.1M diethyl ether·BF_3 in dichloromethane (5 mL, 0.5 mmol) to give, after 2 h, an oily residue which was treated in oxolane (10 mL) with tetrabutylammonium fluoride trihydrate (0.80 g, 2.54 mmol) for 3 h. The mixture was purified on silica gel by flash chromatography (7:3, v/v, petroleum ether–ethyl acetate); yield 0.32 g (47%) of **5**, colorless oil [in addition to **4** (0.10 g, 15%)]; R_F (7:3, v/v, petroleum ether–ethyl acetate) 0.21; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.59–6.88 (m, 20 H, 4 C_6H_5), 6.19 (bs, 1 H, OH), 5.93, 5.86 (2.65, 2 H, H-2,6), 5.11–3.39 (m, 15 H, 4 CH_2, 7 sugar H), 3.62, and 3.56 (2 s, 6 H, 2 OMe).

Anal. Calc. for $C_{42}H_{44}O_8$ (676.8): C, 74.54; H, 6.55. Found: C, 74.36; H, 6.69.

*2-Acetoxy-4,6-dimethoxy-1-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)benzene* (**6**). — Compound **4** (0.21 g, 0.31 mmol) was dissolved in 1:1 (v/v) methanol–ethyl acetate (6 mL). After addition of Pd–C (80 mg), hydrogenation was monitored by t.l.c. (4:1, v/v, chloroform–methanol). After completion of the reaction, filtration and evaporation of the solvent gave a liquid residue which was dissolved in 1:1 acetic anhydride–2-methylpyridine (2 mL) at room temperature. After 17 h, the mixture was treated with water (50 mL), and then extracted three times with dichloromethane (20 mL). The organic layer was washed two times with M HCl (20 mL) and then evaporated. The oily residue was purified on silica gel by flash chromatography (2:3, v/v, petroleum ether–ethyl acetate). For analysis purposes,

the material was again purified on silica gel by elevated pressure chromatography with the same solvent system; yield 0.14 g (84%), amorphous solid, $[\alpha]_{578}^{23}$ −43° (*c* 1, chloroform), R_F (2:3, v/v, petroleum ether–ethyl acetate) 0.53; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 6.31, 6.22 (2 d, 2 H, $J_{4,6}$ 2.5 Hz, H-4,6), 5.70–5.65 (m, 1 H, H-2′), 5.30–5.10 (m, 2 H, H-3′,4′), 4.85 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.40–4.00 (m, 2 H, H-6′,6″), 3.70 (cm, 1 H, H-5′), 3.81, 3.76 (2 s, 6 H, 2 OMe), 2.34 (s, 3 H, $COCH_3$), 2.04, 2.02, 1.99, and 1.75 (4 s, 12 H, 4 $COCH_3$).

Anal. Calc. for $C_{24}H_{30}O_{13}$ (526.5): C, 54.75; H, 5.74. Found: C, 54.77; H, 5.68.

*Methyl 3-[2,4,6-trimethoxy-3-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-phenyl]propionate* (**7**). — (*a*) *Synthesis of methyl 3-(2,4,6-trimethoxyphenyl)propionate.* Methyl 2,4,6-trimethoxycinnamate[23] (0.70 g, 2.77 mmol) was dissolved in methanol (30 mL) and hydrogenated after addition of PtO_2 (150 mg). After completion of the reaction, filtration and evaporation gave a solid residue that was purified on silica gel by elevated pressure chromatography (4:1, v/v, petroleum ether–ethyl acetate); yield 0.43 g (61%), amorphous solid, R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.58; ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 6.11 (s, 2 H, H-3,5), 3.79 (s, 3 H, OMe), 3.78 (s, 6 H, 2 OMe), 3.66 (s, 3 H, CO_2Me), 2.99–2.82 (m, 2 H, β-CH_2), and 2.53–2.34 (m, 2 H, α-CH_2).

Anal. Calc. for $C_{13}H_{18}O_5$ (254.3): C, 61.41; H, 7.14. Found: C, 61.26; H, 7.16.

(*b*) *Synthesis of* **7**. As described for the preparation of **2**, procedure (*a*) was applied to **1** (0.91 g, 1.33 mmol), methyl 3-(2,4,6-trimethoxyphenyl)-propionate (0.30 g, 1.18 mmol) in anhydrous dichloromethane (10 mL), and 0.1M diethyl ether · BF_3 in dichloromethane (8 mL, 0.80 mmol) to give an oily residue that was purified on silica gel by flash chromatography (7:3, v/v, petroleum ether–ethyl acetate); yield 0.12 g of unreacted propionate and 0.44 g of **3** (80%, relative to used **1**), colorless oil, R_F (7:3, v/v, petroleum ether–ethyl acetate) 0.53; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.34–6.83 (m, 20 H, 4 C_6H_5), 6.27, 6.22 (2s, 1 H, H-5), 4.98–4.43 (m, 9 H, 4 C_6H_5–CH_2, 1 sugar H), 4.14, 4.02 (2 d, 1 H, $J_{1',2'}$ 10.6 Hz, H-1′), 3.91–3.55 (m, 5 H, 5 sugar H), 3.83, 3.82, 3.81, 3.77, 3.73, 3.70, 3.69, 3.62 (6 s, 12 H, 4 OMe), 2.96–2.78 (m, 2 H, β-CH_2), and 2.58–2.41 (m, 2 H, α-CH_2).

This material was directly transformed into **8**.

*Methyl 3-[2,3,6-trimethoxy-3-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl]propionate* (**8**). — This compound was obtained from **7** (0.23 g, 0.30 mmol) as described for the preparation of **6**; yield 0.13 g (74%) colorless oil; R_F (2:3, v/v, petroleum ether–ethyl acetate) 0.49; ^{1}H-n.m.r. [250 MHz, ($^2H_6$)Me_2SO, 130°]: δ 6.42 (s, 1 H, H-5), 5.76 (dd, 1 H, $J_{1',2'}$ 9.8, $J_{2',3'}$ 9.6 Hz, H-2′), 5.21 (dd, 1 H, $J_{2',3'}$ 9.6, $J_{3',4'}$ 9.3 Hz, H-3′), 4.99 (dd, 1 H, $J_{3',4'}$ 9.3, $J_{4',5'}$ 9.8 Hz, H-4′), 4.89 (d, 1 H, $J_{1',2'}$ 9.8 Hz, H-1′), 4.10 (cm, 2 H, H-6′,6″), 3.93–3.86 (m, 1 H, H-5′), 3.80, 3.72, 3.59 (3 s, 12 H, 4 OMe), 2.79 (cm, 2 H, α-CH_2), 2.43 (cm, 2 H, β-CH_2), 1.99, 1.95, 1.91, and 1.66 (4 s, 12 H, 4 $COCH_3$).

Anal. Calc. for $C_{27}H_{36}O_{14}$ (584.6): C, 55.48; H, 6.21. Found: C, 55.27; H, 6.30.

2-[2,4,6-Trimethoxy-3-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)phenyl]-1-propene (**9**) *and 3-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-2-(2,4,6-trimethoxyphenyl)-1-propene* (**12**). — As described for the preparation of **2**, procedure (*a*) applied to **1** (0.53 g, 0.77 mmol), 2-(2,4,6-trimethoxyphenyl)-1-propene[24] (0.15 g, 0.72 mmol) in anhydrous dichloromethane (8 mL), and 0.56M diethyl ether·$ZnCl_2$ in dichloromethane (6 mL, 3.36 mmol) gave, after 1 h, and oily residue that was purified on silica gel by flash chromatography (4:1 v/v, petroleum ether–ethyl acetate). Separation of the isomers was performed by elevated pressure chromatography on silica gel (19:1, v/v, toluene–ethyl acetate) to give **9** (0.21 g, 39%), **6**, and **12** (0.21 g, 39%), colorless oils.

Compound **9**. $[\alpha]_{578}^{23}$ +18° (*c* 1, chloroform), R_F (19:1, v/v, toluene–ethyl acetate)0.14; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.36–6.97 (m, 20 H, 4 C_6H_5), 6.27 (s, 1 H, H-5), 5.84 (d, 1 H, $J_{1',2'}$ 7.3 Hz, H-1'), 5.32, 4.94 (2 cm, 2 H, $=CH_2$), 4.81–4.26 (m, 8 H, 4 $C_6H_5CH_2$), 4.05 (dd, 1 H, $J_{1',2'}$ 7.3, $J_{2',3'}$ 7.3 Hz), 4.03–3.95 (m, 1 H, H-5'), 3.82 (s, 3 H, OMe), 3.72 (s, 6 H, 2 OMe), 3.80–3.62 (m, 4 H, H-3',4',6',6''), and 2.05 (s, 3 H, C–CH_3).

Anal. Calc. for $C_{46}H_{50}O_8$ (730.9): C, 75.59; H, 6.90. Found: C, 75.38; H, 6.99.

Compound **12**. $[\alpha]_{578}^{23}$ +38° (*c* 1, chloroform), R_F (19:1, v/v, toluene–ethyl acetate) 0.15; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.34–7.12 (m, 20 H, 4 C_6H_5), 6.11 (s, 2 H, H-3,5), 5.41 [cm, 1 H, =CH (*Z*)], 4.99 [(d, 1 H, *J* 1.8 Hz, =CH (*E*)], 4.93–4.44 (m, 8 H, 4 C_6H_5–CH_2), 4.34–4.22 (m, 1 H, H-1'), 3.80 (s, 3 H, OMe), 3.70 (s, 6 H, 2 OMe), 3.78–3.49 (m, 6 H, 6 sugar H), and 2.89–2.68 (m, 2 H, C–CH_2–C).

Anal. Calc. for $C_{46}H_{50}O_8$ (730.9): C, 75.59; H, 6.90. Found: C, 75.39; H, 7.03.

2-Hydroxy-4,6-dimethoxy-3-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)acetophenone (**10**). — As described for the preparation of **2**, procedure (*a*) applied to **1** (0.59 g, 0.85 mmol), 2-hydroxy-4,6-dimethoxyacetophenone[25] (0.17 g, 0.89 mmol) in anhydrous dichloromethane (10 mL), and $ZnCl_2$ (0.24 g, 1.75 mmol) gave, after 3 h, an oily residue that was purified on silica gel by flash chromatography (3:2, v/v, petroleum ether–ethyl acetate) and then on silica gel by elevated pressure chromatography (9:1, v/v, toluene–acetone); yield 0.09 g (17%), colorless oil, $[\alpha]_{578}^{23}$ +16° (*c* 1, chloroform); R_F (3:2, v/v, petroleum ether–ethyl acetate) 0.41; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 14.30 (bs, 1 H, OH), 6.03 (s, 1 H, H-6), 6.01 (d, 1 H, $J_{1',2'}$ 7 Hz, H-1'), 5.00–3.70 (m, 14 H, 4 C_6H_5–CH_2, 6 sugar H), 3.94, 3.88 (2 s, 6 H, 2 OMe), and 2.65 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{44}H_{47}O_9$ (719.9): C, 73.42; H, 6.58. Found: C, 73.63; H, 6.55.

1,2,3-Trimethoxy-4-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)benzene (**13**). — As described for the preparation of **2**, procedure (*a*) applied to **1** (0.67 g, 0.97 mmol), 1,2,3-trimethoxybenzene[26] (0.33 g, 1.94 mmol) in anhydrous dichloromethane (5 mL), and $ZnCl_2$ (0.35 g, 2.57 mmol) gave, after 6 h, an oily residue that

was purified on silica gel by flash chromatography (1:1, v/v, petroleum ether–diethyl acetate); yield 0.11 g (17%), colorless oil, R_F (1:1, v/v, petroleum ether–diethyl acetate) 0.37; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 7.75–7.20 (m, 20 H, 4 C_6H_5), 6.90–6.70 (m, 2 H, H-5,6), 5.86 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1'), 5.18–3.75 (m, 14 H, 4 C_6H_5–CH_2, and 6 sugar H), and 3.93 (bs, 9 H, 3 OMe).

Anal. Calc. for $C_{43}H_{46}O_8$ (690.8): C, 74.76; H, 6.71. Found: C, 74.52; H, 6.83.

*3,4,5-Trimethoxy-2-(2,3,4,6-tetra-*O*-benzyl-β-* (**14**) *and -α-*D*-glucopyranosyl)-toluene.* — As described for the preparation of **2**, procedure (*a*) applied to **11** (0.87 g, 0.95 mmol), 3,4,5-trimethoxytoluene (0.30 mL, 1.78 mmol) in anhydrous dichloromethane (10 mL), and 0.1M diethyl ether·BF_3 in dichloromethane (10 mL, 1.0 mmol) gave, after 1 h, an oily residue that was purified on silica gel by flash chromatography, and then by elevated pressure chromatography (4:1, v/v, petroleum ether–ethyl acetate), **14** (0.28 g, 47%) and its α-D anomer (20 mg, 3%).

Compound **14**. Colorless oil, rotamers, R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.39; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): **10** δ 7.32–6.92 (m, 20 H, 4 C_6H_5), 6.50, 6.46 (2 s, 1 H, H-6), 4.95–4.43 (m, 8 H, 4 C_6H_5–CH_2), 4.13–3.74 (m, 7 H, 7 sugar H), 3.85, 3.83, 3.81, 3.80 (4s, 9 H, 3 OMe), 2.47–2.26 (3s, 3 H, C–CH_3).

Anal. Calc. for $C_{44}H_{48}O_8$ (704.9): C, 74.98; H, 6.86. Found: C, 74.46; H, 6.92.

*α-*D *Anomer of* **14**. Colorless oil, $[\alpha]_{578}^{23}$ +23° (*c* 1, chloroform), R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.46; ^{1}H-n.m.r. (250 MHz, $CDCl_3$):δ 7.31–7.00 (m, 20 H, 4 C_6H_5), 6.48 (s, 1 H, H-6), 5.53 (d, 1 H, $J_{1',2'}$ 3.2 Hz, H-1'), 4.72–4.16 (m, 8 H, 4 C_6H_5–CH_2), 4.00–3.71 (m, 6 H, 6 sugar H), 3.86, 3.78, 3.66 (3 s, 9 H, 3 OMe), 2.60 (s, 3 H, C–CH_3).

Anal. Calc. for $C_{44}H_{48}O_8$ (704.9): C, 74.98, H, 6.86. Found: C, 74.87; H, 7.00.

*3,4,5-Trimethoxy-2-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)toluene* (**15**). — As described for the preparation of compound **6**, **14** (0.28 g, 0.40 mmol) gave **15** (0.18 g, 88%), colorless oil as rotamers, $[\alpha]_{578}^{25}$ −14° (*c* 1, chloroform), R_F (3:2, v/v, petroleum ether–ethyl acetate) 0.24; ^{1}H-n.m.r. [250 MHz, ($^2H_6$)Me_2SO, 100°]: δ 6.54 (s, 1 H, H-6), 5.51 (dd, 1 H, $J_{1',2'}$ 9.5, $J_{2',3'}$ 9.5 Hz, H-2'), 5.27 (dd, 1 H, $J_{2',3'}$ 9.5, $J_{3',4'}$ 9.5 Hz, H-3'), 5.04 (dd, 1 H, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.8 Hz, H-4'), 4.93 (d, 1 H, $J_{1',2'}$ 9.5 Hz, H-1'), 4.14 (cm, 2 H, H-6',6''), 3.99–3.96 (m, 1 H, H-5'), 3.80, 3.77, 3.71 (3 s, 9 H, 3 OMe), 2.35 (s, 3 H, C–CH_3), 2.00, 1.98, 1.92, and 1.70 (4 s, 12 H, 4 $COCH_3$).

Anal. Calc. for $C_{24}H_{28}O_{12}$ (508.5): C, 56.69; H, 6.55. Found: C, 56.29; H, 6.32.

*1,2,4-Trimethoxy-5-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)benzene* (**16**). — As described for the preparation of **2**, procedure (*a*) applied to **1** (0.60 g, 0.87 mmol), 1,2,4-trimethoxybenzene (0.13 mL, 0.77 mmol) in anhydrous dichloromethane (10 mL), and $ZnCl_2$ (0.01 g, 0.70 mmol) gave, after 4 h an oily residue that was purified on silica gel by flash chromatography and elevated pressure

chromatography (3:1, v/v, petroleum ether–ethyl acetate); yield 0.25 g (47%), colorless oil $[\alpha]_{578}^{23}$ +4.5° (*c* 1, chloroform); R_F (7:3, v/v, petroleum ether–ethyl acetate) 0.35; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 7.75–7.10 (m, 21 H, 4 C_6H_5, H-6), 6.70 (s, 1 H, H-3), 5.20–3.60 (m, 15 H, 4 C_6H_5–CH_2, 7 sugar H), 3.95, 3.83, and 3.80 (3 s, 9 H, 3 OMe).

Anal. Calc. for $C_{43}H_{46}O_8$ (690.8): C, 74.76; H, 6.71. Found: C, 74.75; H, 6.85.

*1,2,4-Trimethoxy-5-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)benzene* (**17**). — As described for the preparation of compound **6**, **16** (0.14 g, 0.20 mmol) gave **17** (66 mg, 73%), colorless foam, $[\alpha]_{578}^{23}$ −18° (*c* 1, chloroform), R_F (3:2, v/v, petroleum ether–ethyl acetate) 0.46; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 6.88 (s, 1 H, H-6), 6.49 (s, 1 H, H-3), 5.50–5.20 (m, 3 H, H-2′,3′,4′), 4.90 (d, 1 H, $J_{1',2'}$ 9.8 Hz, H-1′), 4.32–4.08 (m, 2 H, H-6′,6″), 3.90–3.75 (m, 1 H, H-5′), 3.89, 3.85, 3.82 (3 s, 9 H, 3 OMe), 2.07, 2.06, 2.01 (3 s, 9 H, 3 $COCH_3$), and 1.79 (s, 3 H, CH_3CO).

Anal. Calc. for $C_{23}H_{30}O_{12}$ (498.5): C, 55.42; H, 6.07. Found: C, 55.48; H, 6.13.

*2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-*D*-glucopyranose* (**18**). — A solution of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-D-glucose orthoacetate[17] (31.7 g, 94.14 mmol) in anhydrous methanol (100 mL) was treated at 0° with anhydrous NH_3 gas. After 2 h, the mixture was evaporated to complete dryness. The residue was dissolved in anhydrous *N,N*-dimethylformamide (250 mL). To the solution at 0° and under a N_2 atmosphere, NaH (11.60 g, 483.3 mmol) was added. When the formation of H_2 had ceased, benzyl bromide (48.5 mL, 483.3 mmol) was added slowly with strong stirring. In order to complete the benzylation, additional NaH (4.0 g, 0.167 mol) and benzyl bromide (20 mL, 0.2 mol) were added after 12 h. Slow addition of methanol (20 mL) and then water (500 mL) ended the reaction. The organic material was extracted with chloroform (3 × 100 mL), the organic phase dried ($MgSO_4$), and evaporated. The oily residue was purified by chromatography on silica gel, which had been activated by treatment with HNO_2 (7:3, v/v, petroleum ether–ethyl acetate). This material was pure enough for further reactions; yield 30.25 g (74%), viscous oil. Addition of 7:2 (v/v) petroleum ether–ethyl acetate gave the α-D anomer as crystalline material, m.p. 124–126°, $[\alpha]_{578}^{23}$ +64° (*c* 1, chloroform); R_F (7:3, v/v, petroleum ether–ethyl acetate) 0.32; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.36–7.09 (m, 15 H, 3 C_6H_5), 5.40 (cm, 1 H, H-1), 4.88 (dd, 1 H, $J_{1,2}$ 2.7, $J_{2,3}$ 10.7, H-2), 4.83–4.47 (m, 6 H, 3 C_6H_5–CH_2), 4.11–4.01 (m, 2 H, H-3,4), 3.72–3.58 (m, 3 H, H-5,6,6′), 3.18 (bd, 1 H, OH), and 2.03 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{29}H_{31}O_7$ (491.6): C, 70.86; H, 6.36. Found: C, 70.61; H, 6.49.

*3,4,6-Tri-*O*-benzyl-*D*-glucopyranose* (**19**). — A solution of **18** (10.0 g, 20.34 mmol) in anhydrous methanol (200 mL) was treated at 0° with anhydrous NH_3 gas for 4 h and, after 12 h at room temperature, the solvent was evaporated and the residue chromatographed on silica gel (1:1, v/v, petroleum ether–ethyl acetate); yield 1.73 g (84%), amorphous solid, R_F (3:2, v/v, petroleum ether–ethyl acetate) 0.13; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.36–7.08 (m, 15 H, 3 C_6H_5), 5.36 (bs, 0.5 H,

H-1), 5.20 (cm, 0.5 H, H-1α), 4.93–4.75 (m, 3 H, 1.5 C_6H_5–CH_2), 4.64 (bs, 0.5 H, H-1), 4.57–4.41 (m, 3.5 H, 1.5 C_6H_5–CH_2, H-1β), 4.04–3.41 (m, 6 H, 6 sugar H), and 2.76 (d, 0.5 H, *J* 6.4 Hz, H-2α).

Anal. Calc. for $C_{27}H_{30}O_6$ (450.5): C, 71.98; H, 6.71. Found: C, 71.84; H, 6.75.

*3,4,6-Tri-*O*-benzyl-1,2-di-*O*-(3,4,5-trimethoxybenzoyl)-α,β-*D*-glucopyranose* (**20**). — To a solution of **19** (6.74 g, 14.96 mmol) and 2-methylpyridine (10 mL, 102.76 mmol) in anhydrous dichloromethane (5 mL) and toluene (15 mL) was added, at 0°, 3,4,5-trimethoxybenzoyl chloride[27] (10.13 g, 49.95 mmol) dissolved in toluene (10 mL). After 2 h, the mixture was poured onto ice–water (150 mL) and then extracted with dichloromethane (3 × 40 mL). The organic phase was washed with M NaOH (50 mL) and M HCl (50 mL), dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography on silica gel (3:2, v/v, petroleum ether–ethyl acetate); yield 9.67 g (77%), colorless oil. The anomers were separated by elevated pressure chromatography with the same solvent system.

α-D Anomer. $[\alpha]_{578}^{23}$ +137° (*c* 1, chloroform), R_F t.l.c. (3:2, v/v, petroleum ether–ethyl acetate) 0.62; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.38–7.09 (m, 19 H, aryl H), 6.62 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.47 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.9 Hz, H-2), 4.91–4.52 (m, 6 H, 3 C_6H_5–CH_2), 4.19 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 8.8 Hz, H-3), 4.03–3.52 (m, 4 H, H-4,5,6,6'), 3.91, 3.86, 3.85 (3 s, 12 H, 4 OMe), and 3.64 (s, 6 H, 2 OMe).

Anal. Calc. for $C_{47}H_{50}O_{14}$ (838.9): C, 67.29; H, 6.01. Found: C, 67.35; H, 6.24.

β-D Anomer. $[\alpha]_{578}^{23}$ +1.1° (*c* 1, chloroform), R_F (3:2, v/v, petroleum ether–ethyl acetate) 0.51; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.34–7.25 (m, 19 H, aryl H), 5.92 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 5.59 (dd, 1 H, $J_{1,2}$ 8.2 Hz, $J_{2,3}$ 8.2 Hz, H-2), 4.87–4.50 (m, 6 H, 3 C_6H_5–CH_2), 4.00–3.67 (m, 5 H, 5 sugar H), 3.88 (s, 12 H, 4 OMe), and 3.84 (s, 6 H, 2 OMe).

Anal. Calc. for $C_{47}H_{50}O_{14}$ (838.9): C, 67.29; H, 6.01. Found: C, 67.38; H, 6.14.

*3,4,6-Tri-*O*-benzyl-2-*O*-(3,4,6-trimethoxybenzoyl)-*D*-glucopyranose* (**21**). — In analogy to the procedure of Excoffier *et al.*[28], a solution of **20** (4.23 g, 5.14 mmol) and hydrazine acetate (1.10 g, 11.82 mmol) in anhydrous *N,N*-dimethylformamide (20 mL) was warmed to 55° for 4 h and kept at room temperature for 2 h. Then ethyl acetate (70 mL) was added and the mixture poured on a saturated NaCl solution (30 mL). The organic phase was extracted with ethyl acetate (2 × 30 mL), dried, and the solvent evaporated. The solid residue was crystallized from ethanol. The mother liquor was purified by chromatography on silica gel (3:2, v/v, petroleum ether–ethyl acetate); yield 2.38 g (72%), colorless crystals, m.p. 167°; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.35–7.14 (m, 17 H, aryl H), 5.58 (m, 1 H, H-1), 5.09 (dd, 1 H, $J_{1,2}$ 2.3, $J_{2,3}$ 9.8 Hz, H-2), 4.85–4.50 (m, 6 H, 3 C_6H_5–CH_2), 4.23 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.2 Hz, H-3), 4.15 (m, 1 H, H-5), 3.90 (s, 3 H, OMe), 3.83 (s, 6 H, 2 OMe), 3.74–3.66 (m, 3 H, H-4,6,6'), and 3.05 (m, 1 H, OH).

Anal. Calc. for $C_{37}H_{40}O_{10}$ (644.7): C, 68.93; H, 6.25. Found: C, 68.74; H, 6.44.

3,4,6-Tri-O-benzyl-2-O-(3,4,5-trimethoxybenzoyl)-α- and -β-D-glucopyranosyl trichloroacetimidate (**22**). — To a solution of **21** (0.38 g, 0.59 mmol) and trichloroacetonitrile (1 mL, 9.97 mmol) in anhydrous dichloromethane (25 mL) was added, at room temperature, anhydrous K_2CO_3 (4.0 g). The mixture was stirred for 19 h and then NaH (20 mg) added. After 3 h, the solid material was filtered off and the solvent evaporated. The oily residue was purified by flash chromatography on silica gel (7:3, v/v, petroleum ether–ethyl acetate) (an analytical sample was purified by elevated pressure chromatography on silica gel with the same solvent system) to give 0.38 g (81%) of α-D anomer and 0.08 g (17%) of β-D anomer.

α-D-Anomer. $[\alpha]_{578}^{23}$ +8° (*c* 1, chloroform), R_F (7:3, v/v, petroleum ether–ethyl acetate) 0.71; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 8.53 (s, 1 H, NH), 7.37–7.16 (m, 17 H, aryl H), 6.65 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.43 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.2 Hz, H-2), 4.90–4.51 (m, 6 H, 3 C_6H_5–CH_2), 4.26 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 10.2 Hz, H-3), 4.09–3.76 (m, 4 H, 4 sugar H), 3.92 (s, 3 H, OMe), and 3.84 (s, 6 H, 2 OMe).

Anal. Calc. for $C_{39}H_{40}Cl_3NO_{10}$ (789.1): C, 59.36; H, 5.11; N, 1.78. Found: C, 58.94; H, 5.35; N, 1.50.

β-D Anomer. $[\alpha]_{578}^{23}$ +64° (*c* 1, chloroform), R_F (7:3, v/v, petroleum ether–ethyl acetate) 0.51; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 8.61 (s, 1 H, NH), 7.37–7.12 (m, 17 H, aryl H), 5.95 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.54 (cm, 1 H, H-5), 4.86–4.54 (m, 6 H, 3 C_6H_5–CH_2), 3.94–3.75 (m, 5 H, 5 sugar H), 3.91 (s, 3 H, OMe), and 3.86 (s, 6 H, 2 OMe).

(3R,4R,4aR,10bS)-3,4-Diacetoxy-2-acetoxymethyltetrahydropyrano[5,6-c]-3,4-dihydroisocoumarin (**24**). — As described for the preparation of **2**, procedure (*a*) applied to the α-D anomer of **22** (0.24 g, 0.30 mmol) in anhydrous toluene (30 mL) and 0.1M diethyl ether·BF_3 in anhydrous dichloromethane (5 mL, 0.5 mmol) gave, after 2 h, an oily residue. This was purified by flash chromatography on silica gel (3:2, v/v, petroleum ether–ethyl acetate) to give a material (0.20 g) that contained **23** and **26**. As described for compound **6**, this material was transformed into compounds **24** and **27**, which were separated by flash chromatography on silica gel (2:3, v/v, petroleum ether–ethyl acetate) to give **24** (50 mg, 35%) and **27** (26 mg, 20%). Compound **24** showed m.p. 212° (ethanol), $[\alpha]_{578}^{23}$ −9.1° (*c* 1, chloroform), R_F (2:3, v/v, petroleum ether–ethyl acetate) 0.26; ^{1}H-n.m.r. (400 MHz, CD_3CN): δ 7.26 (s, 1 H, H-7), 5.42 (dd, 1 H, $J_{3,4}$ 9.5, $J_{4,4a}$ 9.5 Hz, H-4), 5.10 (d, 1 H, $J_{5,10b}$ 7.8 Hz, H-10b), 5.04 and 4.98 (m, 2 H, H-3,4a), 4.12–4.05 (m, 2 H, CH_AH_BOAc), 3.86–3.78 (m, 1 H, H-2), 3.86 (s, 6 H, 2 OMe), 3.80 (s, 3 H, OMe), 1.93, 1.89, 1.84 (3 s, 9 H, 3 $COCH_3$); [250 MHz; 9:1, v/v, ($^2H_6$)acetone–$CDCl_3$] δ 7.28 (s, 1 H, H-7), 5.44 (dd, 1 H, $J_{3,4}$ 9.5, $J_{4,4a}$ 9.5 Hz, H-4), 5.28 (d, 1 H, $J_{4a,10b}$ 7.9 Hz, H-10b), 5.10 (dd, 1 H, $J_{4a,10b}$ 7.9, $J_{4,4a}$ 9.5 Hz, H-4a), 5.06 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 9.5 Hz, H-3), 4.19 (dd, 1 H, J_{2,H_A} 5.2, J_{H_A,H_B} 12.8 Hz, CH_AH_BOAc), 3.98 (dd, 1 H, J_{2,H_B} <1, J_{H_A,H_B} 12.8 Hz, CH_AH_BOAc), 3.89 (s, 6 H, 1 OMe), 3.83 (s, 3 H, OMe), 3.87–3.80 (m, 1 H, H-2), 1.98, 1.90, and 1.87 (3 s, 9 H, 3 $COCH_3$); ^{13}C-n.m.r. (100 MHz, $CDCl_3$): δ 170.2, 170.0, 169.8 (3 s, 3 C, 3 $COCH_3$), 164.2 (s, 1 C, aryl *C*O), 152.8 (s, 2 C, C-8,10), 142.5 (s, 1 C, C-9), 124.1 (s, 2 C, C-6a,10a), 107.2 (d, 1 C, C-7), 96.9, 72.2, 72.1, 71.3, 69.1 (5 d, 5 C, 5 pyranose C), 61.7 (t, CH_2OAc), 60.7

(q, 1 C, OMe-4), 56.1 (q, 2 C, OMe-3,4), and 20.4 (q, 3 C, 3 CO–CH_3); m.s.: *m/z* 483 (M + H^+) and 195 (100%).

Anal. Calc. for $C_{22}H_{26}O_{12} \cdot 0.5\ H_2O$ (491.446): C, 53.76; H, 5.54. Found: C, 53.62; H, 5.43.

3,4,6-Tri-O-benzyl-1-N-(trichloroacetyl)-2-O-(3,4,5-trimethoxybenzoyl)-β-D-glucopyranosylamine (**25**). — As described for the preparation of **2**, procedure (*a*) applied to the α-D anomer of **22** (1.06 g, 1.34 mmol) in anhydrous hexane–dichloromethane (12 mL, 5:1, v/v) and trifluoromethanesulfonic acid (0.50 mL, saturated solution) gave, after 3 h, and oily residue that was purified by flash chromatography on silica gel (7:3, v/v, petroleum ether–ethyl acetate); yield 0.71 g (67%) colorless oil, $[\alpha]_{578}^{23}$ +82° (*c* 1, chloroform), R_F (7:3, v/v, petroleum ether–ethyl acetate) 0.45; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.62 (d, 1 H, *J* 7.6 Hz, NH), 7.62–7.17 (m, 17 H, aryl H), 5.23 (cm, 2 H, H-1,2), 4.86–4.50 (m, 6 H, 3 C_6H_5–CH_2), 3.91 (s, 3 H, OMe), 3.86 (s, 6 H, 2 OMe), and 4.01–3.65 (m, 5 H, 5 sugar H).

Anal. Calc. for $C_{39}H_{40}Cl_3NO_{10}$ (789.1): C, 59.36; H, 5.11; Cl, 13.48; N, 1.78. Found: C, 58.96; H, 5.06; Cl, 13.09; N, 1.75.

1,6-Anhydro-3,4-di-O-benzyl- (**26**) *and 3,4-di-O-acetyl-2-O-(3,4,5-trimethoxybenzoyl)-β-D-glucopyranose* (**27**). — As described for the preparation of **2**, procedure (*a*) applied to the β-D anomer of **22** (0.11 g, 0.14 mmol) in anhydrous dichloromethane (10 mL) and 0.56M diethyl ether · $ZnCl_2$ in dichloromethane (2 mL, 1.12 mmol) gave, after 4 h, an oily residue. This was purified by flash chromatography and elevated pressure chromatography on silica gel (7:3, v/v, petroleum ether–ethyl acetate) to give **26** (20 mg, 27%) and **21** (50 mg, 55%).

Compound **26**. Colorless oil $[\alpha]_{578}^{23}$ +17.5° (*c* 1, chloroform); R_F (7:3, v/v, petroleum ether–ethyl acetate) 0.33; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.36–7.25 (m, 12 H, aryl H), 5.58 (cm, 1 H, H-1), 5.00 (cm, 1 H, H-2), 4.85 (d, 1 H, *J* 12.0 Hz, C_6H_5–CH-4), 4.71–4.70 (m, 1 H, H-5), 4.61 (d, 1 H, *J* 12.0 Hz, C_6H_5–CH-4), 4.50 (s, 2 H, C_6H_5–CH_2-3), 4.16–4.13 (m, 1 H, sugar H), 3.87–3.45 (m, 2 H, 2 sugar H), 3.91 (s, 3 H, OMe), and 3.80 (s, 6 H, 2 OMe).

Anal. Calc. for $C_{30}H_{32}O_9$ (536.6): C, 67.15; H, 6.01. Found: C, 67.38; H, 6.12.

Compound **26** was transformed into compound **27** as described for the preparation of compound **24**; yield 74%, colorless foam, $[\alpha]_{578}^{23}$ +50° (*c* 1, chloroform); R_F (2:3, v/v, petroleum ether–ethyl acetate) 0.46; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.35 (s, 2 H, aryl H), 5.58 (cm, 1 H, H-1), 5.08 (cm, 1 H, H-3), 4.82 (cm, 1 H, H-2), 4.71 (cm, 1 H, H-4), 4.67 (cm, 1 H, H-5), 4.16 (dd, 1 H, $J_{5,6} < 1$, $J_{6,6'}$ 7.3 Hz, H-6), 3.92 (s, 9 H, 3 OMe), 3.86 (dd, 1 H, $J_{5,6'}$ 5.5, $J_{6,6'}$ 7.3 Hz, H-6'), 2.16, and 2.13 (2 s, 6 H, 2 $COCH_3$).

Anal. Calc. for $C_{20}H_{24}O_{11}$ (440.4): C, 54.55; H, 5.49. Found: C, 54.47; H, 5.50.

1,3-Dimethoxy-4-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)benzene[11,29] (**29**). — As described for the preparation of **2**, procedure (*a*) applied to **1** (0.85 g, 1.2 mmol), 1,3-dimethoxybenzene (0.17 g, 1.2 mmol) in anhydrous dichloro-

methane (20 mL), and 0.5M diethyl ether·BF_3 in dichloromethane (0.5 mL, 0.25 mmol) gave an oily residue that was purified by elevated pressure chromatography on silica gel (3:2, v/v, petroleum ether–diethyl acetate); yield 0.60 g, (76%), colorless crystals, $[\alpha]_{578}^{23}$ +15.6° (*c* 1, chloroform); ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.40–6.85 (m, 21 H, 4 C_6H_5, H-5), 6.57–6.45 (m, 2 H, H-2,6), 4.99–3.92 (m, 8 H, 4 CH_2) 3.81 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), and 3.82–3.52 (m, 6 H, 6 sugar H).

Anal. Calc. for $C_{42}H_{44}O_7$ (660.8): C, 76.34; H, 6.71. Found: C, 76.26; H, 6.70.

*1,3-Dihydroxy-4-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)benzene* (**30**). — As described for the preparation of **2**, procedure (*a*) applied to **1** (2.0 g, 2.9 mmol), 1,3-bis(trimethylsilyloxy)benzene (0.75 g, 2.9 mmol) in anhydrous dichloromethane (30 mL), and 0.5M diethylether·BF_3 in dichloromethane (2 mL, 1.0 mmol) gave an oily residue that was treated with 0.2N H_2SO_4 (30 mL) at reflux for 8 h to remove the silyl groups. This mixture was made neutral, concentrated, the organic material extracted with dichloromethane (2 × 50 mL), and the solvent evaporated. Purification by elevated pressure chromatography on silica gel (4:1, v/v, petroleum ether–ethyl acetate) yielded a colorless oil (1.01 g, 54%), R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.23; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.40–7.05 (m, 21 H, 4 C_6H_5, H-5), 6.70–6.46 (m, 2 H, H-2,6), 5.18–4.55 (m, 9 H, 4 CH_2, H-1′), and 3.97–3.58 (m, 6 H, 6 sugar H).

Anal. Calc. for $C_{40}H_{40}O_7$ (632.7): C, 75.93; H, 6.37. Found: C, 75.75; H, 6.29.

1-Hydroxymethyl-3,5-dimethoxy-2- (**32**) *and -4-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)benzene* (**35**). — (*a*) *Synthesis of (1,1-dimethylethyl)diphenylsilyl 3,5-dimethoxybenzyl ether.* This compound was prepared according to a general procedure[22] from 3,5-dimethoxybenzyl alcohol; yield 63%, slightly yellow oil; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 7.72–7.25 (m, 10 H, 2 C_6H_5), 6.51–6.31 (m, 3 H, H-2,4,6), 4.72 (s, 2 H, CH_2), 3.76 (s, 6 H, 2 OMe), and 1.10 (s, 9 H, CMe_3); m.s.: *m/z* 349 (M^+ − *tert.*butyl), 151 (100%).

(*b*) *Synthesis of* **32** *and* **35**. As described for the preparation of **2**, procedure (*a*) applied to **1** (0.94 g, 1.37 mmol), (1,1-dimethylethyl)diphenylsilyl 3,5-dimethoxybenzyl ether (0.64 g, 1.57 mmol) in anhydrous dichloromethane (10 mL), and 0.1M diethyl ether·BF_3 (5 mL, 0.5 mmol) gave after 4 h, an oily residue that was purified on silica gel by flash chromatography (19:1, v/v, toluene–ethyl acetate). This material (0.47 g, 45%), a mixture of **31** and **34** was desilylated with tetrabutylammonium fluoride trihydrate (0.48 g, 1.52 mmol) in oxolane (10 mL), at first at 0° and then for 4 h at room temperature. The mixture was treated with water (100 mL) and extracted with dichloromethane (2 × 50 mL). The organic phase was dried, the solvent evaporated, and the oily residue purified by flash chromatography on silica gel (1:1, v/v, petroleum ether–ethyl acetate) to yield **32** (176 mg, 51%) and **35** (103 mg, 30%).

Compound **32**. Colorless oil, $[\alpha]_{578}^{23}$, +7.8° (*c* 1, chloroform), R_F (1:1, v/v, petroleum ether–ethyl acetate) 0.65; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.37–6.90 (■,

20 H, 4 C_6H_5), 6.57, 6.37 (2 d, 2 H, *J* 2.4 Hz, H-2,4), 5.63 (d, 1 H, $J_{1',2'}$ 2.4 Hz, H-1'), 5.03–4.06 (m, 10 H, 4 C_6H_5–CH_2OH), 4.24–3.68 (m, 6 H, 6 sugar H), 3.84 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), and 3.77 (cm, 1 H, H-2'); ^{13}C-n.m.r. (22.6 MHz, $CDCl_3$): δ 160.2, 259.1 (C-3,5), 143.0 (C-1), 138.9, 138.5, 138.4 [C-1 (C_6H_5)], 128.2, 128.1, 127.9, 127.4, 127.2, 127.1 (C_6H_5), 114.6 (C-2), 103.4, 102.3 (C-4, C-6), 87.4, 79.9, 79.6, 75.7, 75.0, 74.3, 73.1, 72.6, 69.1 (4 C_6H_5–CH_2, 5 pyranose C), 65.2 (–CH_2OH), 56.1, and 55.8 (2 OCH_3).

Anal. Calc. for $C_{43}H_{46}O_8$ (690.8): C, 74.76; H, 6.71. Found: C, 74.42; H, 6.89.

Compound **35**. Colorless oil, $[\alpha]_{578}^{23}$ −2.5° (*c* 1, chloroform), R_F (1:1, v/v, petroleum ether–ethyl acetate) 0.38; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.37–6.86 (M, 20 H, 4 C_6H_5), 6.59, 6.62 (2 s, 2 H, H-2,6), 5.00 (d, 1 H, $J_{1',2}$ 10.1 Hz; H-1'), 4.97–4.05 (m, 8 H, 4 C_6H_5–CH_2), 4.41 (dd, 1 H, $J_{1',2'}$ 10.1, $J_{2',3'}$ 8.5 Hz, H-2'), 3.93–3.74 (m, 4 H, H-3',4',6',6''), 3.80 (s, 3 H, OMe), 3.72 (s, 3 H, OMe), 3.57 (cm, 1 H, H-5'), and 1.80 (bs, 1 H, OH).

Anal. Calc. for $C_{43}H_{46}O_8$ (690.8): C, 74.76; H, 6.71. Found: C, 74.70; H, 6.64.

*3,5-Dimethoxy-2-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)benzyl acetate* (**33**). — As described for the preparation of compound **6**, **32** (0.13 g, 0.19 mmol) gave **33** (63 mg, 61%), colorless oil, $[\alpha]_{578}^{23}$ −10.5° (*c* 1, chloroform), R_F (2:3, v/v, petroleum ether–ethyl acetate) 0.62; ^{1}H-n.m.r. [400 MHz; ($^2H_6$)Me_2SO, 140°]: δ 6.53, 6.52 (2 s, 2 H, H-4,6), 5.47 (dd, 1 H, $J_{2',3'}$ 9.5, $J_{3',4'}$ 9.6 Hz, H-3'), 5.26 (d, 1 H, *J* 12.6 Hz, C*H*–OAc) 5.24 (dd, 1 H, $J_{1',2'}$ 9.9, $J_{2',3'}$ 9.5 Hz, H-2'), 5.16 (d, 1 H, *J* 12.6 Hz, C*H*–OAc), 5.02 (dd, 1 H, $J_{3',4'}$ 9.6, $J_{4',5'}$ 9.8 Hz, H-4'), 5.01 (d, 1 H, $J_{1',2'}$ 9.9 Hz, H-1'), 4.12 (cm, 2 H, H-6',6'', 3.91 (cm, 1 H, H-5'), 3.80, 3.77 (2 s, 6 H, 2 OMe), 2.07, 1.99, 1.97, 1.91, and 1.68 (5 s, 15 H, 5 $COCH_3$).

Anal. Calc. for $C_{25}H_{32}O_{13}$ (540.5): C, 55.55; H, 5.97. Found: C, 55.29; H, 6.06.

*2,2-Dimethyl-7-methoxy-6-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)-2*H*-chromen* (**36**). — As described for the preparation of **2**, procedure (*a*) applied to **1** (0.96 g, 1.40 mmol), 2,2-dimethyl-7-methoxy-2*H*-chromen (Precocene I: 0.29 g, 1.53 mmol) in anhydrous nitromethane (6 mL), and $ZnCl_2$ (0.35 g, 2.56 mmol) gave, after 1 h, an oily residue that was purified by flash chromatography on silica gel (19:1, v/v, toluene–ethyl acetate), yield 0.40 g (40%), colorless crystals, m.p. 107–108°; $[\alpha]_{578}^{23}$ +0.4° (*c* 1, chloroform); R_F (19:1, v/v, toluene–ethyl acetate) 0.43; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.33–6.91 (m, 20 H, 4 C_6H_5), 7.06 (s, 1 H, H-5), 6.38 (s, 1 H, H-8), 6.28 (d, 1 H, $J_{3,4}$ 9.8 Hz, H-4), 5.48 (d, 1 H, $J_{3,4}$ 9.8 Hz, H-3), 4.99–4.51 (m, 4 H, 2 C_6H_5–CH_2), 4.45 (dd, 1 H, $J_{1',2'}$ 10.3, $J_{2',3'}$ 10.3 Hz, H-2'), 4.01 (d, 1 H, $J_{1',2'}$ 10.3 Hz, H-1'), 3.81–3.60 (m, 9 H, 2 C_6H_5–CH_2, 5 sugar H), 3.72 (s, 3 H, OMe), 1.45, and 1.42 (2 s, 6 H, 2 Me).

Anal. Calc. for $C_{46}H_{48}O_7$ (712.9): C, 77.50; H, 6.79. Found: C, 77.54; H, 6.77.

*2,2-Dimethyl-7-methoxy-6-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)chro-*

man (**37**). — As described for the synthesis of compound **6**, **36** (0.23 g, 0.32 mmol) gave **37** (0.13 g, 76%) after flash chromatography on silica gel (7:3, v/v, petroleum ether–ethyl acetate); colorless foam, $[\alpha]_{578}^{23}$ −18° (*c* 1, chloroform), R_F (same solvent system) 0.57; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 7.04 (s, 1 H, H-8), 6.29 (s, 1 H, H-5), 5.30–5.20 (m, 3 H, H-2′,3′,4′), 4.88 (d, 1 H, $J_{1',2'}$ 9.5 Hz, H-1′), 4.35–4.05 (m, 2 H, H-6′,6″), 3.90–3.75 (m, 1 H, H-5′), 3.76 (s, 3 H, OMe), 2.69 (cm, 2 H, H-4), 2.08, 2.05, 1.78 (4 s, 12 H, $COCH_3$), 1.77 (cm, 2 H, H-3), 1.34, and 1.29 (2 s, 6 H, 2 Me).

Anal. Calc. for $C_{26}H_{35}O_{11}$ (523.6): C, 59.65; H, 6.74. Found: C, 59.58; H, 6.79.

*1,3-Dimethoxy-4-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)naphthalene* (**38**), *rotamers* **a** *and* **b**. — As described for the preparation of **2**, procedure (*a*) applied to **1** (1.19 g, 1.74 mmol), 1,3-dimethoxynaphthalene (0.35 mL, 1.86 mmol) in anhydrous dichloromethane (10 mL), and 0.56M diethylether·$ZnCl_2$ in dichloromethane (10 mL, 5.6 mmol) gave, after 30 min, an oily residue. This was purified by flash chromatography and elevated pressure chromatography on silica gel (4:1, v/v, petroleum ether–ethyl acetate) to yield **38a** (0.40 g, 32%) and **38b** (0.15 g 12%).

Rotamer **a**. $[\alpha]_{578}^{23}$ +27.0° (*c* 1, chloroform), R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.38; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 8.71 (d, 1 H, $J_{7,8}$ 8.2 Hz, H-8), 8.17 (dd, 1 H, $J_{5,6}$ 8.2, $J_{5,7}$ 1.1 Hz, H-5), 7.40–6.98 (m, 22 H, 4 C_6H_5, H-6,7), 6.59 (s, 1 H, H-2), 6.04 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1′), 4.99–4.35 (m, 6 H, 3 C_6H_5–CH_2), 4.13–4.06 (m, 3 H, C_6H_5–CH_2, H-3′), 4.01 (s, 3 H, OMe), 3.92 (cm, 1 H, H-2′), 3.78 (s, 3 H, OMe), and 3.81–3.74 (m, 4 H, H-4′,5′,6′,6″).

Rotamer **b**. $[\alpha]_{578}^{23}$ +27.6° (*c* 1, chloroform), R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.33; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 8.53–8.49 (m, 1 H, H-8), 8.21–8.18 (m, 1 H, H-5), 7.35–7.05 (m, 22 H, 4 C_6H_5, H-6,7), 6.77–6.73 (m, 1 H, H-2), 5.43 (d, 1 H, $J_{1',2'}$ 9.9 Hz, H-1′), 4.99–4.48 (m, 6 H, 3 C_6H_5–CH_2), 4.27 (dd, 1 H, $J_{1',2'}$ 9.9, $J_{2',3'}$ 9.9 Hz, H-2′), 4.18–3.56 (m, 7 H, C_6H_5–CH_2, 5 sugar H), 4.03, and 3.89 (2 s, 6 H, 2 OMe).

Anal. Calc. for $C_{46}H_{46}O_7$ (710.9): C, 77.72; H, 6.92. Found (mixtures of rotamers): C, 77.48; H, 6.48.

*1,3-Dimethoxy-4-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)naphthalene* (**39**). — As described for the preparation of compound **6**, **38** (rotamer **a**) (0.32 g, 0.42 mmol) gave **39** (0.15 g, 69%), after flash chromatography on silica gel (1:1, v/v, petroleum ether–ethyl acetate), colorless oil, R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.43; ^{1}H-n.m.r. [250 MHz; ($^2H_6$–Me_2SO) 129°]: δ 8.30 (d, 1 H, $J_{7,8}$ 8.6 Hz, H-8), 8.08 (dd, 1 H, $J_{5,6}$ 8.2, $J_{5,7}$ 0.9 Hz, H-5), 7.55–7.44 (m, 1 H, H-7), 7.29 (dd, 1 H, $J_{5,6}$ 8.2, $J_{6,7}$ 8.9 Hz, H-6), 6.79 (s, 1 H, H-2), 5.67 (dd, 1 H, $J_{2',3'}$ 9.6, $J_{3',4'}$ 9.6 Hz, H-3′), 5.49 (d, 1 H, $J_{1',2'}$ 9.8 Hz, H-1′), 5.36 (dd, 1 H, $J_{3',4'}$ 9.6, $J_{4',5'}$ 9.6 Hz, H-4′), 5.21 (dd, 1 H, $J_{1',2'}$ 9.8, $J_{2',3'}$ 9.6 Hz, H-2′), 4.21–3.92 (m, 3 H, H-5′,6′,6″), 4.01, 3.95 (2 s, 6 H, 2 OMe), 2.03, 1.99, 1.91, and 1.55 (4 s, 12 H, 4 $COCH_3$).

Anal. Calc. for $C_{23}H_{30}O_{11}$ (482.5): C, 57.26; H, 6.27. Found: C, 57.49; H, 6.39.

10-(2,3,3,6-Tetra-O-benzyl-α,β-D-glucopyranosyl)anthrone (**40**). — (*a*) *Synthesis of 9-trimethylsilyloxyanthracene*. As described for the preparation of 3,5-dimethoxy-1-trimethylsilyloxybenzene from anthrone, 9-trimethylsilyloxyanthracene was obtained in 85% yield, b.p. 120° (1 MPa); ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 8.56–8.13 (m, 5 H, H-1,4,5,8,10), 7.58 (m, 4 H, H-2,3,6,7), 0.35 (s, 9 H, $SiMe_3$); m.s.: *m/z* 266 (M^+) and 73 (100%).

(*b*) *Synthesis of* **40**. As described for the preparation of **2**, procedure (*a*) applied to **1** (0.79 g, 1.15 mmol), 9-trimethylsilyloxyanthracene (0.37 g, 1.38 mmol) in anhydrous dichloromethane (5 mL), and 0.25M diethyl ether·BF_3 in dichloromethane (4.20 mL, 1.1 mmol) gave, after 4 h, an oily residue that was purified by flash chromatography and elevated pressure chromatography on silica gel (4:1, v/v, petroleum ether–ethyl acetate); yield 0.33 g (40%) of a 1:1 mixture of the anomers which could not be separated; R_F (4:1, v/v, petroleum ether–ethyl acetate) 0.60; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 8.30 (m, 2 H, H-1,8), 7.90–7.20 (m, 26 H, aryl H), and 5.02–3.25 (m, 16 H, 4 CH_2, 7 sugar H, and H-10).

Anal. Calc. for $C_{48}H_{44}O_6$ (116.9): C, 80.42; H, 6.19. Found: C, 80.24; H, 6.31.

10-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)anthrone (**41**). — As described for the preparation of **2**, procedure (*a*) applied to compound **42**[19] (2.20 g, 4.50 mmol), 9-trimethylsilyloxyanthracene (1.40 g, 5.30 mmol) in anhydrous dichloromethane (10 mL), and $SnCl_4$ (0.52 mL, 2.74 mmol) gave, after 1 h, a solid residue that was purified by flash chromatography and elevated pressure chromatography on silica gel (3:2, v/v, petroleum ether–ethyl acetate); yield 0.79 g (34%), yellow powder, m.p. 137–138° (methanol–water), $[\alpha]_{578}^{23}$ −10.6° (*c* 1, chloroform); R_F (3:2, v/v, petroleum ether–ethyl acetate) 0.39; ^{1}H-n.m.r. (250 MHz, $CDCl_3$): δ 8.21 (m, 2 H, H-1,8), 7.64–7.34 (m, 6 H, H-2,7), 5.08 (dd, 1 H, $J_{2',3'}$ 9.2, $J_{3',4'}$ 9.7 Hz, H-3'), 4.73 (dd, 1 H, $J_{3',4'}$ 9.7, $J_{4',5'}$ 10.1 Hz, H-4'), 4.66 (dd, 1 H, $J_{1',2'}$ 10.1, $J_{2',3'}$ 9.2 Hz, H-2'), 4.41 (d, 1 H, *J* 1.5 Hz, H-10), 4.03–3.86 (m, 3 H, H-1',6',6''), 3.51–3.44 (m, 1 H, H-5'), 2.02, 1.96, 1.91, and 1.90 (4 s, 12 H, 4 $COCH_3$).

Anal. Calc. for $C_{28}H_{28}O_{20}$ (524.5): C, 64.12; H, 5.76. Found: C, 64.37; H, 5.84.

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