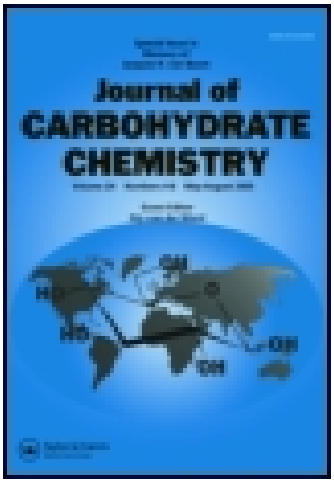

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STUDIES ON THE FAST ATOM BOMBARDMENT MASS SPECTROMETRY FRAGMENTATION OF AMINO SUGARS USING SYNTHETIC DERIVATIVES OF THE TRISACCHARIDE UNIT β-D-GLUCOPYRANOSYL-(1-3)-*O*-2-DEOXY-2-AMINO-β-D-GLUCOPYRANOSYL-(1-4)-*O*-β-D-GLUCOPYRANOSE

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ABSTRACT

N-Phthaloyl, *N*-acetyl, *N*-benzyl, *N*-acetyl-*N*-methyl, *N,N*-dimethyl, *N*-benzoyl, and *N,N*-dibenzoyl derivatives of the trisaccharide ß-D-glucopyranosyl-(1-3)-*O*-(2-deoxy-2-amino-ß-D-glucopyranosyl)-(1-4)-*O*-ß-D-glucopyranose were synthesized and analyzed by FAB MS. The intensity ratios of the peaks resulting from cleavage of the anomeric bond of the glucosamine residue and the respective molecular ion peaks turned out to be high for the *N*-acyl derivatives and up to two orders of magnitude lower for the *N*-alkyl compounds. These results show that fragmentation at the anomeric carbon of the amino sugar may be assisted by the carbonyl group and the resulting cation is stabilized by delocalization of the positive charge.

INTRODUCTION

The FAB MS analyses of oligosaccharides containing *N*-acetylamino sugars show main fragmentations at the anomeric carbon of the amino sugar:

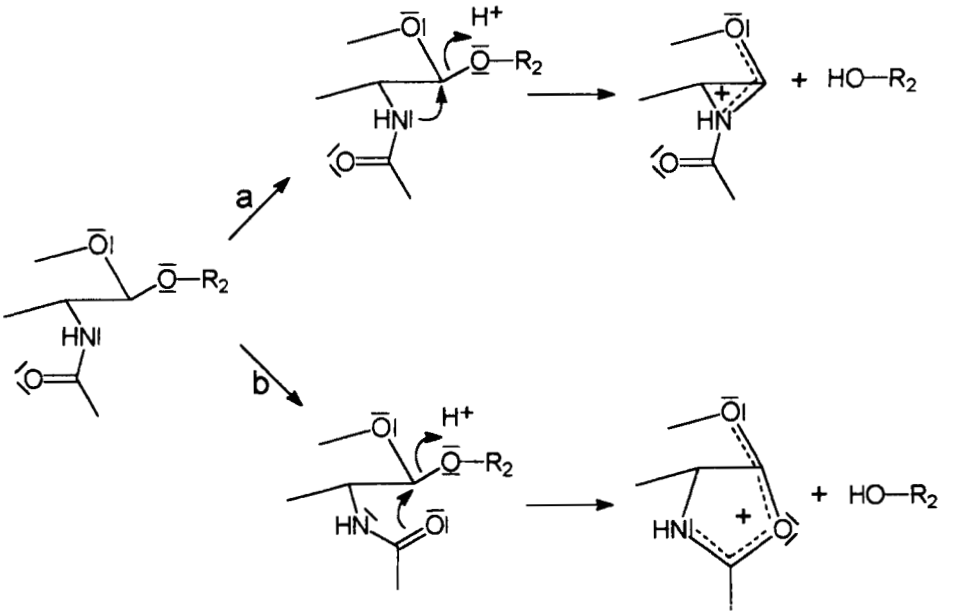
$$R_1\text{-O-HexNAc-O-}R_2 \xrightarrow{H^+} R_1\text{-O-HexNAc}^+ + \text{HO-}R_2$$

These fragmentations usually produce the most intense peaks in the FAB spectra. Two possible pathways have been proposed for the preferred fragmentation:

a) the free electron pair of the nitrogen facilitates the separation of residue R_2 by a neighbouring group effect,

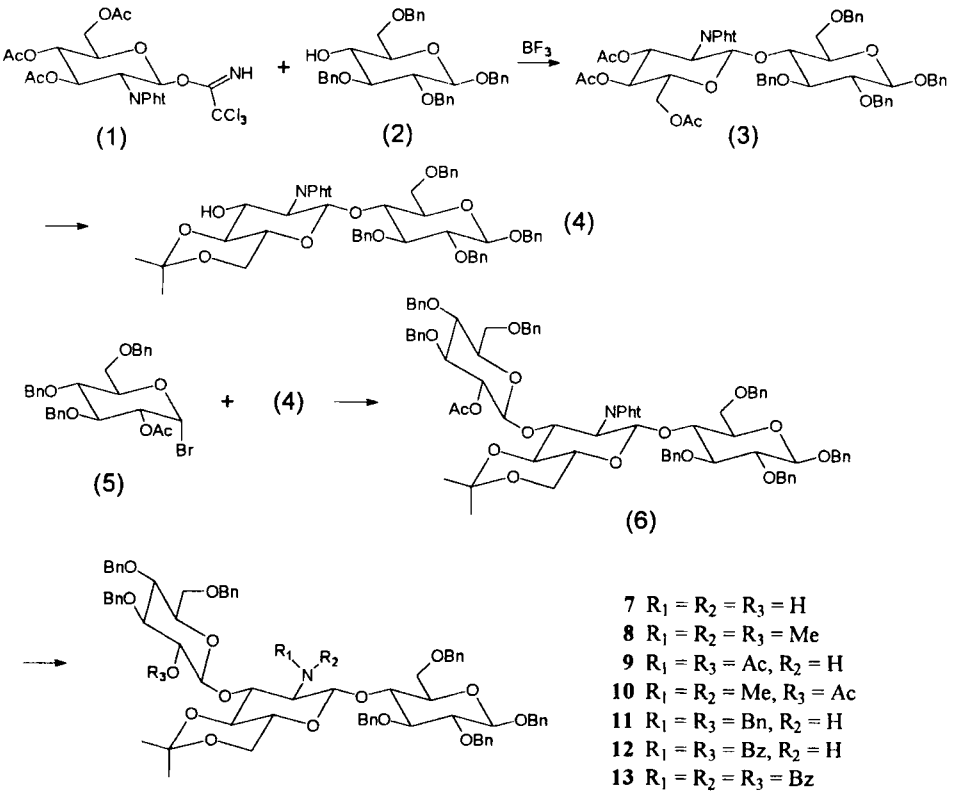
b) first an free electron pair of the carbonyl oxygen assists cleavage of the "aglycon" and then the resulting cation is stabilized by additional delocalisation of the positive charge (five membered ring).

In order to examine the influence of the nitrogen substituents on the formation and the stability of the fragment ion, -NPht, -NHAc, -NHBn, -NMeAc, -NMe_2, -NHBz, and -NBz_2 derivatives of the trisaccharide ß-D-glucopyranosyl-(1-3)-*O*-(2-deoxy-2-amino-ß-D-glucopyranosyl)-(1-4)-*O*-ß-D-glucopyranose were synthesized and analysed by FAB MS.



RESULTS AND DISCUSSION

Synthesis of the trisaccharide derivatives. Compound **2** was obtained in 81% yield[2] after reduction of benzyl 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-ß-D-glucopyranoside[1] with sodium cyanoborohydride. Glycosylation of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-



ß-D-glucopyranosyl trichloroacetimidate[5] with the glycosyl acceptor **2** in dichloromethane at 0 °C using boron trifluoride etherate as promoter[6] gave the disaccharide **3** in 72%. After Zemplén deacetylation of **3** and isopropylidenation with 2,2-dimethoxypropane and *p*-toluenesulfonic acid in DMF[7], the glycosyl acceptor **4** was obtained in a yield of 68%.

Glycosylation of the glycosyl acceptor **4** with the bromide **5**[9] in dichloromethane using mercuric(II) cyanide/mercuric(II) bromide (5:2) as promoter[8] gave the trisaccharide **6** in 48% yield. Treatment of **6** with hydrazine hydrate in boiling 90% aqueous ethanol gave the derivative **7**. Starting from this trisaccharide the other derivatives were prepared. Methylation of **7** with methyl iodide and sodium hydride in DMF gave **8** in 38% yield. Acetylation of **7** with acetic anhydride and pyridine yielded **9** in 44%. Subsequent methylation of **9** with methyl iodide and sodium hydride in DMF led to **10** in 38 %.

Benzylation of **7** with benzyl bromide and sodium hydride in DMF gave **11** in 38%. Finally, benzoylation of **7** with benzoyl chloride and pyridine gave **12** and **13** with yields of 29% and 24%, respectively.

FAB mass spectrometry. A comparison of the ratio of the relative intensities of the peaks resulting from the fragmentation at the anomeric carbon of the aminoglucose (fragment ion A^+) and the $M+H^+$ ($M+Na^+$) peaks clearly shows the influence of the nitrogen substituents on the stability of this fragment ion. Figure 1 exemplarily shows the spectra obtained from **8** and **13**, respectively.

Compound **13** with two benzoyl groups attached to the nitrogen showed the most stable fragment A^+ ion (see Table). This is probably due to stabilization of the cation **14** by alternative delocalisation of the positive charge over the anomeric rings of both benzoyl groups. This assumption is supported by the fact that the mono-*N*-benzoylated compound **12** as well as the substances **10** and **9** show an about one magnitude lower intensity ratio than **13**. (In fact the spectra of **12** and **13** contain $M+Na^+$ besides $M+H^+$ and for the calculation of the intensity ratios the relative intensities of the peaks for both molecular ions were added. However, the intensities of $M+Na^+$ peaks are generally up to one order of magnitude higher than those observed for $M+H^+$ peaks. Therefore in the absence of sodiated molecular ions the intensity ratios for **12** and **13** might even be higher than those shown in the table.)

At first glance for compound **6**, a result comparable with those obtained for **9**, **10**, **12** and **13** should be expected. But for an efficient delocalization of the positive charge a system of two condensed planar five-membered rings (**15**) has to be formed which is energetically unfavourable. Therefore a considerable stabilisation of the corresponding cation (as was observed for the compounds **9**, **10**, **12** and **13**) is not possible and the peak intensity ratio is one to two orders of magnitude lower than in the spectra of the other *N*-acylated trisaccharides (see Table).

The highest I_{A^+}/I_M for *N*-alkylated derivatives was found with **11**. This can be explained by a stabilisation of the positive charge of the corresponding fragment ion by the π-electrons of the benzene ring.

Again one order of magnitude lower intensity ratios were found for the *N*-unsubstituted and *N*-alkylated trisaccharides **7** and **8**, respectively (see Table). However, the difference in I_{A^+}/I_M between the derivative with the free amino group **7** and the *N*,*N*-dimethyl compound **8** is probably not due to a reduced stabilisation of A^+ in **8** but rather to an enhanced formation of $M+H^+$ ions because of the higher basicity of the dimethylated compound. Thereby the intensity of the molecular ion peak of **8** is increased and the observed I_{A^+}/I_M is lower.

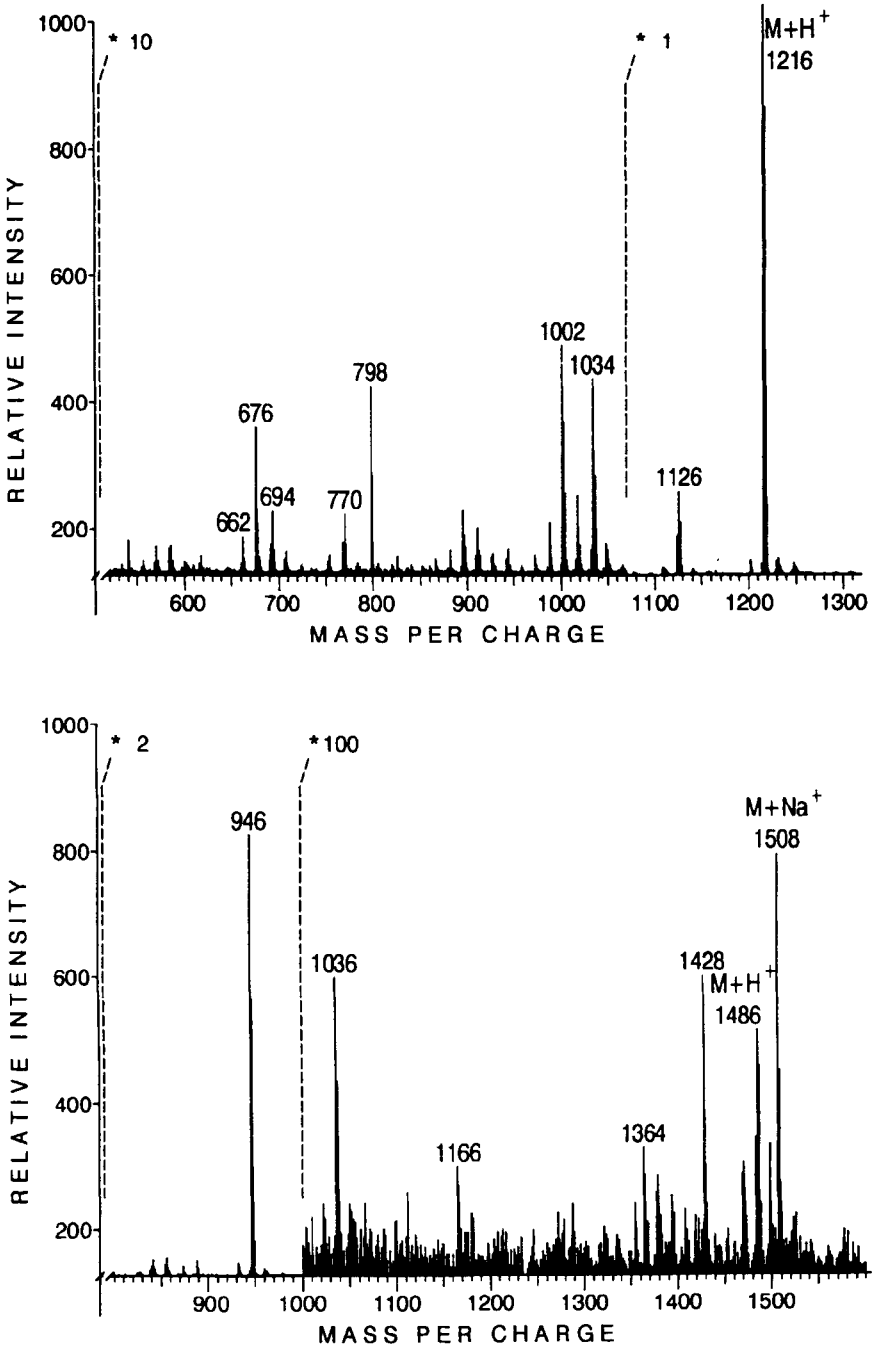
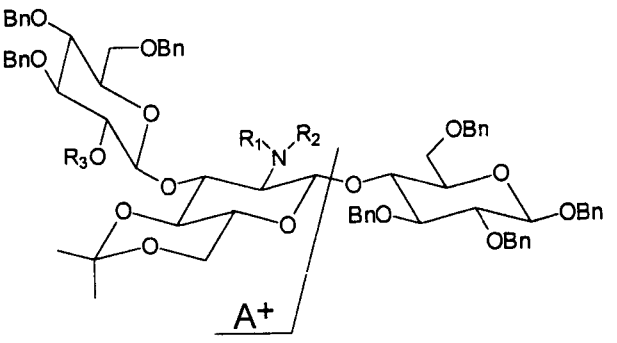


Figure 1. FAB(+) mass spectra of **8** (upper) and **13** (lower)

Table *m/z* values of molecular ions ($M+H^+$ and/or $M+Na^+$) and fragment A ions (A^+) of the dervatives of **7** and the corresponding peak intensity ratios.

Compound	N-Substitution	*m/z* A^+	*m/z* $M+H^+/M+Na^+$	Intensity ratio $\frac{I_{A^+}}{I_M}$
13	NBz_2	946	1486/1508	32.99
12	NHBz	842	1382/1404	4.93
9	NHAc	718	1258	6.85
10	NMeAc	704	1244	2.67
6	NPht	806	1346	0.290
11	NHBn	814	1354	0.215
7	NH_2	634	1174	0.084
8	NMe_2	676	1216	0.025



The results of the FAB MS analyses of **7** and its derivatives show peak intensities for cleavage of the anomeric bonds of the respective aminosugars in the spectra of the *N*-acyl derivatives enhanced by orders of magnitude over those obtained for the corresponding fragmentations of the *N*-alkyl compounds. The stabilisation of the resulting cation is obviously achieved by delocalization of the positive charge in a five-membered ring with participation of the carbonyl group (oxazolidinium structure). On the other hand direct participation of the free electron pair of the nitrogen seems to be unlikely.

EXPERIMENTAL

General methods. Melting points were determined on a Kofler-Weygand melting point apparatus and are uncorrected. The ^{1}H NMR spectra were recorded at 500 MHz with a Bruker AMX-500 spectrometer. The thin-layer chromatograms were performed on precoated plates of silica gel (Merck). Silica gel 60 (400-630 and 630-200 mesh, Merck) was used for column chromatography. All solvents and reagents were purified and dried before use. The molecular sieve was dried for 12 h at 10^{-2} Torr and 140 °C. All glycosylation reactions were performed under an argon atmosphere.

FAB mass spectrometry. The FAB mass spectra were recorded on a VG analytical ZAB-HF reverse geometry mass spectrometer (V.G. Analytical, Manchester, U.K.). For atom bombardment Xenon was used and the applied acceleration voltage was 7 kV. 1-Mercapto-2,3-propanediol (thioglycerol, Tgl) was used as matrix and 1 µL of a homogeneous sample solution containing 1 nmol/µL in chloroform/methanol (1:1 by vol) was added. The spectra were run in a mass range from 50 to 1800 atom mass units (amu) with a scan rate of 10 sec per decade and positive ions (FAB(+)) were detected. The spectra were recorded and evaluated on a SAM II/68 K computer (KWS, Ettlingen, FRG) using the DP10 program of AMD (Harpstedt, FRG).

Benzyl 2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (2). A solution of benzyl 4,6-*O*-benzylidene-2,3-di-*O*-benzyl-ß-D-glucopyranoside[1] and sodium cyanoborohydride in dry tetrahydrofuran containing powdered 3 Å molecular sieves and some methyl orange was cooled to 0 °C.[2] A saturated hydrogen chloride solution in ether was dropped under stirring until the mixture was acidic. After a reaction time of 3 h the mixture was stirred for additional 3 h at room temperature.

The mixture was poured into ice-water (200 mL), and the product was extracted with dichloromethane (3x, 150 mL). The extracts were washed with saturated aqueous sodium hydrogencarbonate, dried over sodium sulfate, filtered and concentrated in vacuo. The product was purified by chromatography on silica gel 60 (light petroleum/ethyl acetate, 25:10, v/v). The product was recrystallized from ethanol/water to give **2** (6.88 g, 81%), mp 66-67 °C (ref.[3,4] 66-67 °C), Rf=0.67 (toluene/acetone, 9:2, v/v). ^{1}H NMR (d_6DMSO): δ 7.40-7.20 (m, 20H, aromat.), 5.38 (d, 1H, J_{OH4}=6.5 Hz, OH), 4.84 (d, 1H, J=12.2 Hz,

CH_2Ph), 4.83 (d, 1H, J=11.5 Hz, CH_2Ph), 4.81 (d, 1H, J=11.5 Hz, CH_2Ph), 4.73 (d, 1H, J=11.5 Hz, CH_2Ph), 4.64 (d, 1H, J=12.0 Hz, CH_2Ph), 4.63 (d, 1H, J=11.5 Hz, CH_2Ph), 4.56 (s, 2H, 2xCH_2Ph), 4.54 (d, 1H, J_{12}=8.4 Hz, H-1), 3.79 (dd, 1H, J_{6a5}=1.4 Hz, J_{6a6b}=11.0 Hz, H-6a), 3.59 (dd, 1H, H_{6b5}=6.0 Hz, J_{6b6a}=11.0 Hz, H-6b), 3.46-3.42 (m, 1H, H-5), 3.41 (t ~ dd, 1H, J_{32}=J_{34}=8.4 Hz, H-3), 3.36 (td, 1H, J_{43}=J_{45}=8.5 Hz, J_{4OH}=6.5 Hz, H-4), 3.26 (t ~ dd, 1H, J_{23}=J_{21}=8.4 Hz, H-2); FAB MS: *m/z* 539 ($M+H^+-H_2$), 433, 341, 325.

Benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (3). A 0.3 M solution of boron trifluoride etherate in dichloromethane (15 mL) was dropped into a mixture of cold (0 °C) **2** (2 g, 3.0 mmol), 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-ß-D-glycopyranosyl trichloroacetimidate[5] (3.48 g, 6.0 mmol) and 4 Å molecular sieves (6 g) in dichloromethane[6] (75 mL). The mixture was stirred for 4 h at 0 °C an then poured into saturated aqueous sodium hydrogencarbonate. The organic phase was washed twice with water (50 mL), dried over sodium sulfate and concentrated in vacuo. The product was purified by chromatography on silica gel 60 (light petroleum/ethyl acetate, 2:1, v/v) to give **3** (2.06 g, 72%), Rf=0.38 (toluene/acetone, 9:1, v/v). ^1H NMR ($CDCl_3$): δ 7.85-7.68 (m, 4H, Pht), 7.40-7.17 (m, 20H, aromat.), 5.69 (d, 1H, J_{12}=8.4 Hz, H-1'), 5.68 (dd, 1H, J_{32}=10.6 Hz, J_{34}=9.1 Hz, H-3'), 5.11 (dd, 1H, J_{43}=9.1 Hz, J_{45}=10.2 Hz, H-4'), 4.96 (d, 1H, J=12.0 Hz, CH_2Ph), 4.93 (d, 1H, J=12.0 Hz, CH_2Ph), 4,84 (2xd, 2x1H, J=10.8 Hz, J=12.0 Hz, 2xCH_2Ph), 4.61 (d, 1H, J=10.8 Hz, CH_2Ph), 4.56 (d, 1H, J=12.0 Hz, CH_2Ph), 4.37 (d, 1H, J_{12}=7.8 Hz, H-1), 4.35 (d, 1H, J=12.0 Hz, CH_2Ph), 4.28 (d, 1H, J=12.0 Hz, CH_2Ph), 4.25 (dd, 1H, J_{21}=8.4 Hz, J_{23}=10.7 Hz, H-2'), 4.03 (dd, 1H, J_{6a5}=3.8 Hz, J_{6a6b}=12.6 HZ, H-6'a), 4.01 (dd, 1H, J_{43}=9.0 Hz, J_{45}=9.8 Hz, H-4), 3.76 (dd, 1H, J_{6b5}=2.3 Hz, J_{6b6a}=12.6 Hz, H-6'b), 3.59 (t ~ dd, 1H, J_{32}=J_{34}=9.0 Hz, H-3), 3.50 (dd, 1H, J_{6a5}=1.8 Hz, J_{6a6b}=11.5 Hz, H-6a), 3.46 (dd, 1H, J_{21}=7.8 Hz, J_{23}=9.0 Hz, H-2), 3.42 (dd, 1H, J_{6b5}=4.2 Hz, J_{6b6a}=11.5 Hz, H-6b), 3.33 (ddd, 1H, J_{54}=10.2 Hz, J_{56a}=2.3 Hz, J_{56b}=3.8 Hz, H-5'), 3.26 (ddd, 1H, J_{54}=9.8 Hz, J_{56a}=1.8 Hz, J_{56b}=4.2 HZ, H-5), 1.98, 1.97, 1.82 (3xs, 3x3H, 3xAc); FAB MS: *m/z* 980 ($M+Na^+$), 890, 782, 418, 358, 298, 256.

Benzyl *O*-(2-deoxy-4,6-*O*-isopropylidene-2-phthalimido-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (4). To a solution of **3** (2.0 g, 2.1 mmol) in dichloromethane/methanol (5 mL, 3:2) a 0.3 M sodium methoxide solution in methanol (1 mL) was added. The mixture was stirred for 3 h at room temperature and neutralized with

amberlite IR-120 (H^+). After concentration in vacuo and codistillation with toluene (twice) the residue was dissolved in DMF (5 mL). To the solution *p*-toluenesulfonic acid (1 mg) and 2,2-dimethoxypropane (1 mL, 8.17 mmol) were added.[7] The mixture was stirred overnight at room temperature, neutralized with triethylamine and concentrated in vacuo. The product was purified on silica gel 60 (light petroleum/ethyl acetate, 2:1, v/v) to give **4** (1.24 g, 68%), Rf=0.47 (toluene/acetone, 9:2, v/v). ^{1}H NMR (d_6DMSO): δ 8.00-7.80 (m, 4H, Pht), 7.40-7.15 (m, 20H, aromat.), 5.59 (d, 1H, J_{OH3}=5.5 Hz, OH), 5.28 (d, 1H, J_{12}=8.7 Hz, H-1'), 4.83 (d, 1H, J=11.2 Hz, C**H**$_2$Ph), 4.73 (3xd, 3x1H, J=11.2 Hz, J=11.2 HZ, J=11.2 Hz, 3xC**H**$_2$Ph), 4.58 (d, 1H, J=11.2 Hz, C**H**$_2$Ph), 4.52 (d, 1H, J=11.2 Hz, C**H**$_2$Ph), 4.49 (d, 1H, J_{12}=8.2 Hz, H-1), 4.26 (s, 2x1H, 2xC**H**$_2$Ph), 4.09 (td, 1H, J_{32}=J_{34}=9.8 Hz, J_{3OH}=5.5 Hz, H-3'), 3.91 (dd, 1H, J_{21}=8.7 Hz, J_{23}=9.8 Hz, H-2'), 3.79 (t ~ dd, 1H, J_{43}=J_{45}=9.3 Hz, H-4), 3.53 (dd, 1H, J_{6a5}=5.2 Hz, J_{6a6b}=10.8 Hz, H-6'a), 3.51-3.45 (m, 2x1H, H-4',3), 3.43-3.31 (m, 3x1H, H-6'b,5,6a), 3.28 (dd, 1H, J_{6b5}=4.2 Hz, J_{6b6a}=10.8 Hz, H-6b), 3.26 (t ~ dd, 1H, J_{21}=J_{23}=8.2 Hz, H-2), 3.01 (td, 1H, J_{54}=J_{56b}=9.8 Hz, J_{56a}=5.2 Hz, H-5'), 1.49, 1.27 (2xs, 2x3H, 2xC**H**$_3$-Isoprop.); FAB MS: *m/z* 894 (M+Na^+), 804, 712, 314, 332, 274, 256.

Benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-ß-D-glucopyranosyl)-(1-3)-*O*-(2-deoxy-4,6-*O*-isopropylidene-2-phthalimido-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (6). A mixture of **4** (500 mg, 574 μmol), mercuric(II)cyanide (133 mg, 525 μmol), mercuric(II)bromide (76 mg, 210 μmol) and 4 Å molecular sieves (1.5 g) in dichloromethane (5 mL) was stirred 3 h under argon.[8] The bromide **5**[9] (573 mg, 1.03 mmol) was added and the mixture was stirred for additional 48 h. The mixture was filtered and the solids were washed with dichloromethane. The organic extracts were washed twice with water (20 mL), three times with aqueous potassium bromide (20 mL) and again twice with water (20 mL).The dichloromethane solution was dried over sodium sulfate and concentrated in vacuo. The product was purified on silica gel 60 (toluene/acetone, 22:1, v/v) to give **11** (370 mg, 48%), Rf=0.53 (toluene/acetone, 9:1, v/v). ^{1}H NMR ($CDCl_3$): δ 7.65-7.15 (m, 39H, arom.), 5.32 (d, 1H, J_{12}=8.5 Hz, H-1'), 4.87 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.84 (d, 1H, J=11.5 Hz, C**H**$_2$Ph), 4.83 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.82 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.71 (dd, 1H, J_{21}=8.4 Hz, J_{23}=9.6 Hz, H-2"), 4.67 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.65 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.61 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.53 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.52 (d, 1H, J_{12}=8.4 Hz, H-1"), 4.51 (d, 1H, J=11.5 Hz, C**H**$_2$Ph), 4.49 (d, 1H, J=11.5 Hz,

CH_2Ph), 4.47 (dd, 1H, J_{32}=10.5 Hz, J_{34}=8.9 Hz, H-3'), 4.46 (d, 1H, J=11.5 Hz, CH_2Ph), 4.37 (d, 1H, J=12.0 Hz, CH_2Ph), 4.34 (d, 1H, J=12.0 Hz, CH_2Ph), 4.33 (d, 1H, J_{12}=7.7 Hz, H-1), 4.31 (d, 1H, J=12.0 Hz, CH_2Ph), 4.21 (dd, 1H, J_{21}=8.5 Hz, J_{23}=10.5 Hz, H-2'), 3.93 (t ~ dd, 1H, J_{43}=J_{45}=9.2 Hz, H-4), 3.73 (t ~ dd, 1H, J_{43}=J_{45}=8.9 Hz, H-4'), 3.73 (dd, 1H, J_{6a5}=3.9 Hz, J_{6a6b}=10.7 Hz, H-6"a), 3.68 (dd, 1H, J_{6b5}=2.0 Hz, J_{6b6a}=10.7 Hz, H-6"b), 3.62 (t ~ dd, 1H, J_{43}=J_{45}=9.2 Hz, H-4"), 3.58 (dd, 1H, J_{6a5}=5.4 Hz, J_{6a6b}=10.8 Hz, H-6'a), 3.5 (t ~ dd, 1H, J_{32}=J_{34}=9.2 Hz, H-3), 3.46-3.39 (m, 4x1H, H-3",2,6'b,6a), 3.31 (ddd, 1H, J_{54}=9.2 Hz, J_{56a}=1.2 Hz, J_{56b}=4.5 Hz, H-5"), 3.29 (dd, 1H, J_{6b5}=4.5, J_{6b6a}=11.0 Hz, H-6b), 3.14 (ddd, 1H, J_{56a}=1.2 Hz, J_{56b}=4.5 Hz, J_{54}=9.2 Hz, H-5), 3.11 (td, 1H, J_{54}=J_{56a}=8.9 Hz, J_{56b}=5.5 Hz, H-5'), 1.52 (s, 3H, Ac), 1.38, 1.23 (2xs, 2x3H, 2xCH_3-Isoprop.); FAB MS: *m/z* 1346 ($M+H^+$), 1256, 806, 475, 256.

Benzyl *O*-(3,4,6-tri-*O*-benzyl-ß-D-glucopyranosyl)-(1-3)-*O*-(2-amino-2-deoxy-4,6-*O*-isopropylidene-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (7). A solution of **6** (300 mg, 220 µmol), hydrazine hydrate (5.5 mL) and 90% aqueous ethanol (55.5 mL) was heated under reflux overnight.[10,11] After cooling to room temperature the solution was concentrated to dryness. The product was purified on silica gel 60 (light petroleum/ethyl acetate, 1:1, v/v) to give **7** (238 mg, 92,3%), Rf=0.39 (toluene/acetone, 9:2, v/v). FAB MS: *m/z* 1174 ($M+H^+$), 1084, 724, 634, 433.

Benzyl *O*-(3,4,6-tri-*O*-benzyl-2-*O*-methyl-ß-D-glucopyranosyl)-(1-3)-*O*-(2-deoxy-2-dimethylamino-4,6-*O*-isopropylidene-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (8). To a solution of **7** (20 mg, 17.0 µmol) and methyl iodide (100 µL) in DMF (500 µL) sodium hydride (8 mg) was added. The reaction mixture was stirred overnight at room temperature, the remaining sodium hydride was destroyed with a few drops of methanol, and the solution was concentrated in vacuo. The product was purified by preparative TLC (light petroleum/ethyl acetate, 3:1, v/v) to give **8** (8 mg, 38.7%), Rf=0.25 (toluene/acetone, 12:1, v/v). ^1H NMR ($CDCl_3$): δ 7.40-7.10 (m, 35H, aromat.), 4.96 (d, 1H, J=12.0 Hz, CH_2Ph), 4.90 (d, 1H, J=11.0 Hz, CH_2Ph), 4.86 (d, 1H, J=11.0 Hz, CH_2Ph, 4.85 (d, 1H, J=10.5 Hz, CH_2Ph), 4.83 (d, 1H, J=11.0 Hz, CH_2Ph, 4.82 (d, 1H, J=11.0 Hz, CH_2Ph, 4.79 (d, 1H, J=10.5 Hz, CH_2Ph, 4.68 (d, 1H, J=11.0 Hz, CH_2Ph, 4.678 (d, 1H, J=12.0 Hz, CH_2Ph, 4.65 (d, 1H, J=12.2 Hz, CH_2Ph, 4.60 (d, 1H, J_{12}=8.2 Hz, H-1"), 4.59 (d, 1H, J=12.2 Hz, CH_2Ph, 4.58 (d, 1H, J_{12}=8.4 Hz, H-1'), 4.57 (d, 1H, J=12.2 Hz, CH_2Ph, 4.54

(d, 1H, J=11.0 Hz, C**H**$_2$Ph, 4.50 (d, 1H, J_{12}=8.0 Hz, H-1), 4.49 (d, 1H, J=12.2 Hz, C**H**$_2$Ph, 3.91 (dd, 1H, J_{6a5}=2.0 Hz, J_{6a6b}=11.0 Hz, H-6a), 3.90 (t ~ dd, 1H, J_{43}=J_{45}=9.0 Hz, H-4), 3.85 (t ~ dd, 1H, J_{32}=J_{34}=9.7 Hz, H-3'), 3.80 (dd, 1H, J_{6b5}=5.6 Hz, J_{6b6a}=11.0 Hz, H-6b), 3.71-3.67 (m, 2x1H, H-4',6"a), 3.65 (dd, 1H, J_{6b5}=2.2 Hz, J_{6b6a}=11.0 Hz, H-6"b), 3.61 (s, 3H, OCH_3), 3.60 (t ~ dd, 1H, J_{32}=J_{34}=8.7 Hz, H-3), 3.58 (dd, 1H, J_{43}=8.2 Hz, J_{45}=9.2 Hz, H-4"), 3.54-3.47 (m, 4H, H-3",6'a,5,2), 3.54 (t ~ dd, 1H, J_{32}=J_{34}=8.2 Hz, H-3"), 3.49 (dd, 1H, J_{21}=8.0 Hz, J_{23}=8.7 Hz, H-2), 3.43 (t ~ dd, 1H, J_{6b5}=J_{6b6a}=10.2 Hz, H-6'b), 3.34 (ddd, 1H, J_{56a}=4.2 Hz, J_{56b}=2.2 Hz, J_{54}=9.2 Hz, H-5"), 3.07 (t ~ dd, 1H, J_{21}=J_{23}=8.2 Hz, H-2"), 2.81 (td, 1H, J_{54}=J_{56b}=10.2 Hz, J_{56a}=5.3 Hz, H-5'), 2.59 (dd, 1H, J_{21}=8.4 Hz, J_{23}=9.7 Hz, H-2'), 2.42 (s, 2x3H, NMe_2), 1.36, 1.28 (2xs, 2x3H, 2xCH_3, isoprop.); FAB MS: *m/z* 1216 ($M+H^+$), 1126, 1034, 1002, 798, 770, 676.

Benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-ß-D-glucopyranosyl)-(1-3)-*O*-(2-acetamido-2-deoxy-4,6-*O*-isopropylidene-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (9). Acetic anhydride (250 µL) was mixed with a solution of **7** (40 mg, 34.1 µmol) in pyridine (500) µL and the mixture was stirred overnight at room temperature. The solution was concentrated in vacuo and the product was purified by preparative TLC (light petroleum/ethyl acetate, 3:1, v/v) to give **9** (19 mg, 44.7%), Rf=0.39 (toluene/acetone, 9:2, v/v). ^{1}H NMR ($CDCl_3$): δ 7.40-7.13 (m, 35H, aromat.), 5.27 (d, 1H, J_{NH2}=7.8 Hz, N**H**Ac), 4.99 (d, 1H, J_{12}=8.2 Hz, H-1'), 4.95 (d, 1H, J=12.2 Hz, C**H**$_2$Ph), 4.90 (dd, 1H, J_{21}=8.4 Hz, J_{23}=9.5 Hz, H-2"), 4.88 (d, 1H, J=11.4 Hz, C**H**$_2$Ph), 4.82 (d, 1H, J=10.8 Hz, C**H**$_2$Ph), 4.80 (d, 1H, J=11.2 Hz, C**H**$_2$Ph), 4.79 (d, 1H, J=11.5 Hz, C**H**$_2$Ph), 4.77 (d, 1H, J=10.8 Hz, C**H**$_2$Ph), 4.69 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.68 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.65 (d, 2x1H, J=12.2 Hz, 2xC**H**$_2$Ph), 4.63 (d, 1H, J_{12}=8.4 Hz, H-1"), 4.60 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.56 (d, 1H, J=10.0 Hz, C**H**$_2$Ph), 4.53 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.46 (d, 1H, J_{12}=7.4 Hz, H-1), 4.15 (dd, 1H, J_{32}=9.5 Hz, J_{34}=9.0 Hz, H-3'), 3.90 (dd, 1H, J_{43}=8.5 Hz, J_{45}=9.8 Hz, H-4), 3.73-3.69 (m, 3x1H, H-6"a,6"b, 6a), 3.68 (t ~ dd, 1H, J_{43}=J_{45}=9.5 Hz, H-4"), 3.62 (dd, 1H, J_{6b5}=4.4 Hz, J_{6b6a}=10.7 Hz, H-6b), 3.61 (t ~ dd, 1H, J_{32}=J_{34}=9.5 Hz, H-3"), 3.56 (t ~ dd, 1H, J_{43}=J_{45}=9.5 Hz, H-4'), 3.55 (dd, 1H, J_{6a5}=5.5 Hz, J_{6a6b}=10.6 Hz, H-6'a), 3.51 (t ~ dd, 1H, J_{32}=J_{34}=8.5 Hz, H-3), 3.47 (dd, 1H, J_{21}=7.4 Hz, J_{23}=8.5 Hz, H-2), 3.45-3.41 (m, 1H, H-5"), 3.37 (ddd, 1H, J_{56a}=2.0 Hz, J_{56b}=4.2 Hz, J_{54}=9.8 Hz, H-5), 3.36 (t ~ dd, 1H, J_{6b5}=J_{6b6a}=9.5 Hz, H-6'b), 3.12 (ddd, 1H, J_{2NH}=7.8 Hz, J_{21}=8.2 Hz, J_{23}=9.5 Hz, H-2'),

3.03 (td, 1H, J_{56a}=5.5 Hz, J_{54}=J_{56b}=9.5 Hz, H-5'), 1.98 (s, 3H, OAc), 1.82 (s, 3H, NHAc), 1.37, 1.30 (2xs, 2x3H, 2xCH_3-Isoprop.); FAB MS: *m/z* 1258 ($M+H^+$), 1216, 1126, 1036, 718, 628, 568, 475.

Benzyl *O*-(3,4,6-tri-*O*-benzyl-2-*O*-methyl-ß-D-glucopyranosyl)-(1-3)-*O*-(2-deoxy-2-*N*-methylacetamido-4,6-*O*-isopropylidene-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (10). To a solution of **9** (15 mg, 12.0 µmol) and methyl iodide in DMF (500 µL) sodium hydride (8 mg) was added. The reaction mixture was stirred overnight at room temperature, the remaining sodium hydride was destroyed with a few drops of methanol, and the solution was concentrated in vacuo. The products were purified by preparative TLC (light petroleum /ethyl acetate, 3:1, v/v) to give **10** (5 mg, 37.9%), Rf=0.47 (toluene/acetone, 9:2,v/v). ^{1}H NMR ($CDCl_3$): δ 7.40-7.10 (m, 35H, aromat.), 4.92 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.90 (d, 1H, J=10.5 Hz, C**H**$_2$Ph), 4.86 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.80 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.79 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.78 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.72 (d, 1H, J=12.3 Hz, C**H**$_2$Ph), 4.71 (d, 1H, J_{12}=8.1 Hz, H-1'), 4.69 (d, 1H, J=10.5 Hz, C**H**$_2$Ph), 4.65 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.53 (d, 2x1H, J=12.0 Hz, 2xC**H**$_2$Ph), 4.49 (d, 1H, J=12.3v Hz, C**H**$_2$Ph), 4.48 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.47 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.44 (d, 1H, J_{12}=8.0 Hz, H-1), 4.37 (d, 1H, J_{12}=8.0 Hz, H-1"), 4.06 (t ~ dd, 1H, J_{43}=J_{45}=9.6 Hz, H-4), 3.80 (t ~ dd, 1H, J_{32}=J_{34}=9.5 Hz, H-3'), 3.74 (t ~ dd, 1H, J_{43}=J_{45}=9.5 Hz, H-4'), 3.69 (dd, 1H, J_{21}=8.1 Hz, 1H, J_{23}=9.5 Hz, H-2'), 3.69-3.59 (m, 5x1H, H-6a',6a" ,6b", 6a,6b), 3.56 (t ~ dd, 1H, J_{43}=J_{45}=9.6 Hz, H-4"), 3.54-3.48 (m, 3x1H, H-2,3",3), 3.45 (s, 3H, OCH_3), 3.40 (t ~ dd, 1H, J_{6b5}=J_{6b6a}=9.5 Hz, H-6b'), 3.36-3.32 (m, 1H, H-5"), 3.32-3.27 (m, 1H, H-5), 2.96 (t ~ dd, 1H, J_{21}=J_{23}=8.0 Hz, H-2"), 2.92 (td, 1H, J_{54}=J_{56b}=9.5 Hz, J_{56a}5.1 Hz, H-5'), 2.78 (s, 3H, NMeAc), 2.12 (s, 3H, NMe**Ac**), 1,38, 1.29 (2xs, 2x3H, 2xCH_3-Isoprop.); FAB MS: *m/z* 1244 ($M+H^+$), 1136, 1028, 780, 704, 258, 240

Benzyl *O*-(2,3,4,6-tetra-*O*-benzyl-ß-D-glucopyranosyl)-(1-3)-*O*-(2-benzylamino-2-deoxy-4,6-*O*-isopropylidene-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (11). To a solution of **7** (20 mg, 17.0 µmol) and benzyl bromide (100 µL) in DMF (500 µL) was added sodium hydride (8 mg). The reaction mixture was stirred overnight at room temperature, unreacted sodium hydride was destroyed with a few drops of methanol, and the solution was concentrated in vacuo. The products were purified by preparative TLC (light petroleum /ethyl acetate, 3:1, v/v) to give **11** (9 mg, 39.1%), Rf=0.49

(toluene/acetone, 12:1,v/v). ^{1}H NMR ($CDCl_3$): δ 7.40-7.10 (m, 45H, aromat.), 4.94 (d, 1H, J=12.5 Hz, C**H**$_2$Ph), 4.90 (d, 1H, J=10.8 Hz, C**H**$_2$Ph), 4.89 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.81 (s, 2x1H, 2xC**H**$_2$Ph), 4.80 (d, 1H, J=10.0 Hz, C**H**$_2$Ph), 4.71 (d, 3x1H, J=11.5 Hz, 3xC**H**$_2$Ph), 4.70 (d, 1H, J_{12}=8.3 Hz, H-1"), 4.66 (d, 1H, J=12.2 Hz, C**H**$_2$Ph), 4.65 (d, 1H, J=12.2 Hz, C**H**$_2$Ph), 4.57 (d, 1H, J=11.5 Hz, C**H**$_2$Ph), 4.55 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.54 (d, 1H, J=10.8 Hz, C**H**$_2$Ph), 4.49 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.48 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.45 (d, 1H, J_{12}=7.4 Hz, H-1), 4.36 (d, 1H, J_{12}=7.8 Hz, H-1'), 4.05 (dd, 1H, J_{6a5}=3.8 Hz, J_{6a6b}=11.0 Hz, H-6a), 4.02 (t ~ dd, 1H, J_{43}=J_{45}=9.0 Hz, H-4), 3.89 (d, 1H, J=13.5 Hz, C**H**$_2$Ph), 3.84 (dd, 1H, J_{6b5}=1.6 Hz, J_{6b6a}=11.0 Hz, H-6b), 3.76 (dd, 1H, J_{6a5}=5, J_{6a6b}=10.5 Hz, H-6a'), 3.76 (d, 1H, J=13.5 Hz, C**H**$_2$Ph), 3.74 (t ~ dd, 1H, $J_{43}J_{45}$=9.7 Hz, H-4'), 3.70-3.65 (m, 2xH, H-6"a,6"b), 3.64 (t ~ dd, 1H, J_{32}= J_{34}=8.3 Hz, H-3"), 3.63 (t ~ dd, 1H, J_{43}=$_{45}$=8.3 Hz, H-4"), 3.55 (t ~ dd, 1H, J_{32}=J_{34}=9.7 Hz, H-3'), 3.51 (t ~ dd, 1H, J_{32}=J_{34}=9.0 Hz, H-3), 3.48 (dd, 1H, J_{23}=9.0 Hz, J_{21}=7.4 Hz, H-2), 3.47 (t ~ dd, 1H, J_{6b5}=J_{6b6a}=10.5 Hz, H-6'b), 3.42 (m, H-5"), 3.37 (t ~ dd, 1H, J_{21}=$_{23}$=8.3 Hz, H-2"), 3.33 (ddd, 1H, J_{54}=9.0 Hz, J_{56a}=3.8 Hz, J_{56b}=1.6 Hz, H-5), 2.98 (td ~ ddd, 1H, J_{54}=J_{56b}=10.5 Hz, J_{56a}=5.0 Hz, H-5'), 2.72 (dd, 1H, J_{21}=7.8 Hz, J_{23}=9.7 Hz, H-2'), 1.39, 1.29 (2xs, 2x3H, 2xCH_3-Isoprop.); FAB MS: *m/z* 1354 ($M+H^+$), 1264, 814, 724, 523, 382, 292.

Benzyl *O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-ß-D-glucopyranosyl)-(1-3)-*O*-(2-benzamido-2-deoxy-4,6-*O*-isopropylidene-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (12) and Benzyl *O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-ß-D-glucopyranosyl)-(1-3)-*O*-(2-deoxy-2-(*N*,*N*-dibenzoylamino)-4,6-*O*-isopropylidene-ß-D-glucopyranosyl)-(1-4)-2,3,6-tri-*O*-benzyl-ß-D-glucopyranoside (13). To a solution of **7** (26 mg, 22.1 µmol) in pyridine (500 µmol) benzoyl chloride (50 µL) was added and the mixture was stirred overnight at room temperature. Aqueous saturated sodium hydrogencarbonate (100 µL) and a catalytical amount of 4-dimethylaminopyridine were added and the mixture was stirred for further 15 min. After extraction with dichloromethane the organic phase was dried over sodium sulfate and concentrated in vacuo. The products were purified by preparative TLC (light petroleum/ethyl acetate, 3:1, v/v) to give **12** (9 mg, 29.5%) and **13** (8 mg, 24.3%). The Rf values were 0.23 for **12** and 0.58 for **13**, both in (toluene/acetone, 12:1, v/v). ^{1}H NMR ($CDCl_3$) (**12**): δ 7.70-6.95 (m, 45H, aromat.), 6.31 (d, 1H, J_{NH2}=7.2 Hz, N**H**Bz), 5.25 (d, 1H, J_{12}=8.3 Hz, H-1'), 5.19 (t ~ dd, 1H, J_{23}=J_{21}=8.4 Hz, H-2"), 4.86 (d, 1H,

J=12.5 Hz, C**H**$_2$Ph), 4.84 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.83 (d, 1H, J=11.5 Hz, C**H**$_2$Ph), 4.81 (d, 1H, J_{12}=8.4 Hz, H-1"), 4.80 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.75 (d, 1H, J=11.5 Hz, C**H**$_2$Ph), 4.65 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.63 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.61 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.56 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.53 (t ~ dd, 1H, J_{32}=J_{34}=9.5 Hz, H-3'), 4.52 (d, 1H, J=10.5 Hz, C**H**$_2$Ph), 4.51 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.50 (d, 1H, J=10.5 Hz, C**H**$_2$Ph), 4.37 (d, 1H, J_{12}=7.4 Hz, H-1), 4.35 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.29 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 3.87 (t ~ dd, 1H, J_{43}=J_{45}=9.4 Hz, H-4), 3.78-3.71 (m, 3x1H, H-6"a,6"b,4"), 3.70 (t ~ dd, 1H, J_{32}=J_{34}=8.4 Hz, H-3"), 3.66 (t ~ dd, 1H, J_{43}=J_{45}=9.5 Hz, H-4'), 3.58 (ddd, 1H, J_{6a5}=5.4 Hz, J_{6a6b}=10.6 Hz, H-6'a), 3.52-3.46 (m, 3x1H, H-5",6a,3), 3.43 (t ~ dd, 1H, J_{21}=J_{23}=7.4 Hz, H-2), 3.39 (t ~ dd, 1H, J_{6b5}=J_{6b6a}=10.6 Hz, H-6'b), 3.36 (dd, 1H, J_{6b5}=4.8 Hz, J_{6b6a}=11.0 Hz, H6b), 3.27-3.14 (m, 3x1H, H-5,2',5'), 1.35, 1.22 (2xs, 2x3H, 2xC**H**$_3$-Isoprop.); FAB MS (**12**): *m/z* 1404 (M+Na$^+$), 1382 (M+H$^+$), 1278, 842, 537, 306. ^{1}H NMR ($CDCl_3$) (**13**): δ 7.80-7.05 (m, 50H, aromat.), 5.35 (d, 1H, J_{12}=8.2 Hz, H-1'), 5.22 (dd, 1H, J_{21}=J_{23}=8.5 Hz, H-2"), 5.00 (d, 1H, J_{12}=8.0 Hz, H-1"), 4.88 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.84 (d, 1H, J=11.0 Hz, C**H**$_2$Ph), 4.83 (dd, 1H, J_{32}=10.0 Hz, J_{34}=8.3 Hz, H-3'), 4.75 (d, 1H, J=10.7 Hz, C**H**$_2$Ph), 4.66 (d, 1H, J=10.7 Hz, C**H**$_2$Ph), 4.63 (d, 1H, J=12.0 Hz, C**H**$_2$Ph), 4.61 (d, 1H, J=10.7 Hz, C**H**$_2$Ph), 4.61-4.48 (m, 8xH, 8xC**H**$_2$Ph), 4.39 (d, 1H, J_{12}=7.6 Hz, H-1), 4.15 (dd, 1H, J_{21}=8.2 Hz, J_{23}=10.0 Hz, H-2'), 4.12 (t ~ dd, 1H, J_{43}=J_{45}=8.7 Hz, H-4), 3.86 (t ~ dd, 1H, J_{43}=J_{45}=9.2 Hz, H-4"), 3.78 (dd, 1H, J_{6a5}=4.0 Hz, J_{6a6b}=11.0 Hz, H-6"a), 3.73 (dd, 1H, J_{6a5}=5.2 Hz, J_{6a6b}=11.0 Hz, H-6'a), 3.69 (dd, 1H, J_{6b5}=2.3 Hz, J_{6b6a}=11.0 Hz, H-6"b), 3.71-3.61 (m, 4xH, H-6"b,4',3",6a), 3.56 (dd, 1H, J_{6b5}=3.8 Hz, J_{6b6a}=11.5 Hz, H-6b), 3.46-3.35 (m, 4x1H, H-2,5",3,6'b), 3.25 (ddd, 1H, J_{54}=8.9 Hz, J_{56a}=0.8 Hz, J_{56b}=3.8 Hz, H-5), 3.14, (td ~ ddd, 1H, J_{54}=J_{56a}=10.0 Hz, J_{56b}=5.2 Hz, H-5'), 1.38, 1.35 (2xs, 2x3H, 2xC**H**$_3$-Isoprop.); FAB MS (**13**): *m/z* 1508 (M+Na$^+$), 1486 (M+H$^+$), 1428, 1036, 946, 537

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