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Highly stereoselective synthesis of α,β-linked, nonreducing disaccharides related to tunicamycin

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Abstract

3,4,6-Tri-*O*-benzoyl-2-(benzoyloxyimino)-2-deoxy-α-D-*arabino*-hexopyranosyl bromide (**2**) reacts with the *O*-protected 2-deoxy-2-phthalimido-β-D-galactosamines **3** and **4** in the presence of silver triflate and *sym*-collidine at $-78°C$, to give α,β-(1 → 1)-linked disaccharides **6a** and **7a** with an excellent selectivity. The 2-oxyimino function was stereospecifically converted into a 2-acetamido group by use of the $LiBH_4$–Me_3SiCl–THF reductive species, furnishing, after acetylation, the α-D-GlcNAc-(1 → 1)-β-D-GalNPhth nonsymmetrical, trehalose type disaccharides **13** and **14** related to tunicamycin (**1**, part A). Similarly, α-D-GlcNAc-(1 → 1)-β-D-GlcNPhth (**15**) was prepared, starting from **2** and **5**. The factors governing the stereoselectivity of the glycosylation reactions were determined.

1. Introduction

The increasing discovery in Nature of trehalose-type compounds possessing biological activity [1], including immunoadjuvant and antitumor activities [2], necessitates the elaboration of practicable methods for their stereocontrolled synthesis. It must, however, be stressed that a stereoselective preparation of a nonreducing disaccharide is complicated by the fact that two anomeric centers are involved in the double glycosidic linkage. Special difficulties concern the synthesis of nonsymmetrical "trehaloses". To this group belong amino sugar antibiotics [3], i.e., the α,α-linked trehalosamine composed of D-glucose and 2-amino-2-deoxy-D-glucose [4], its 3-amino [5] and 4-amino [6] isomers, as well as 2-amino-2-deoxy-α-D-glucopyranosyl α-D-mannopyranoside [7]. The most difficult task, however, is the generation of the α,β-glycosidic linkage existing in nonsymmetrical disaccharides

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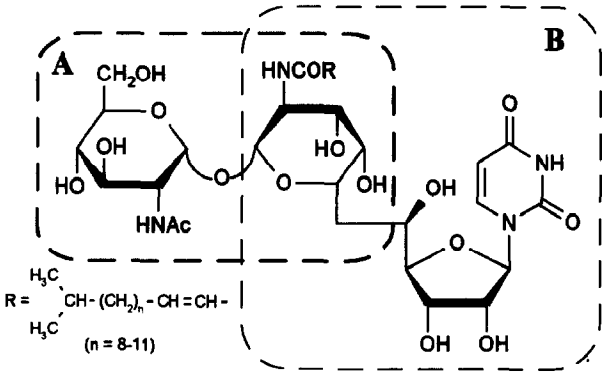
related to α,β-trehalose, illustrated by everninose (2-*O*-methyl-α-L-lyxopyranosyl 2,6-di-*O*-methyl-β-D-mannopyranoside), a common component of the orthomycin antibiotics family [8], by the aminoglycoside antibiotic 3-amino-3-deoxy-α-D-glucopyranosyl 3-amino-3-deoxy-β-D-glucopyranoside [9]; or by the sugar part of the nucleoside antibiotic tunicamycin [10] (formula **1**, part A) where the nonsymmetrical disaccharide is attached to the nucleoside moiety by a C–C linkage.



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The efficient stereocontrolled methods for construction of an α-and/or β-glycosidic linkage [11] have not succeeded in attempts at the stereoselective synthesis of trehalose-type disaccharides. Thus, application of Schmidt's trichloroacetimidate method to the synthesis of everninose gave a mixture of α,β and α,α isomers [12]. Similarly, attachment of a D-glucosamine unit to the tunicaminyluracil moiety (formula **1**, part B), performed by Suami et al. [13], afforded both the desired α,β-glycoside and its β,β anomer. This last coupling failed when applied by Danishefsky's group [14] using the methodology of Suami [13] as well as other glycosylation reactions. Instead, complex mixtures were formed [14].

Motivated by the objective of the synthesis of tunicamycin, we describe herein a highly stereoselective route to the title compounds possessing the 2-amino-2-deoxy-α-D-glucopyranosyl 2-amino-2-deoxy-β-D-galactopyranoside structure (**13** and **14**, the sugar moiety of tunicamycin, part A of **1**), and its 2-amino-2-deoxy-α-D-glucopyranosyl 2-amino-2-deoxy-β-D-glucopyranoside isomer (**15**).

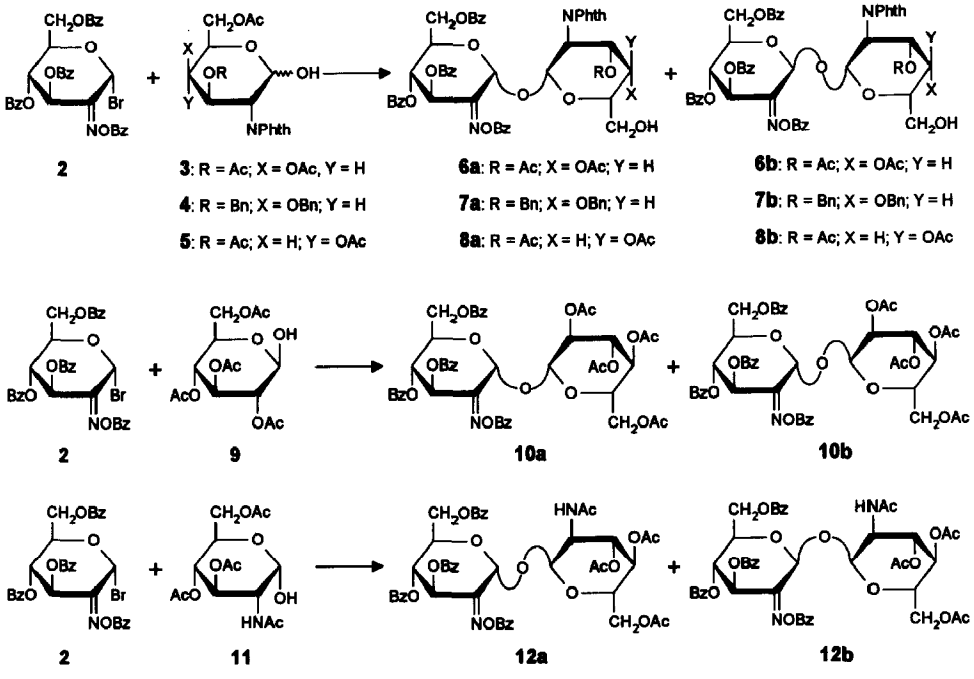
2. Results and discussion

The crucial step of our synthetic strategy, involving the construction of an α,β linkage between two 2-amino-2-deoxyaldopyranoses, both containing equatorial C-2–NHR groups, was based on the idea that the amino sugar acting as the glycosyl donor should have nonparticipating protection at C-2, leading to an α-bond, whereas the amino sugar acting as the acceptor should possess a large C-2 substituent to exert steric hindrance for the α anomer, leading to preferential formation of the β-glycoside. As we have previously reported [15], these conditions require the use of the stable, yet very reactive, 3,4,6-tri-*O*-benzoyl-2-(benzo-

yloxyimino)-2-deoxy-α-D-*arabino*-hexopyranosyl bromide (**2**) [16] (a potential glucosamine moiety) and the 2-deoxy-2-phthalimido derivatives **3–5**. Recently, Myers et al. [17] apparently unaware of our work in this area [15], have reported the stereoselective synthesis of a nonreducing disaccharide composed of α-D-glucosamine and β-D-galactosamine derivatives, involving the same stereodirecting factors.

Condensation of **2** with **3–5** afforded the desired α,β-linked disaccharides **6a–8a** with high stereoselectivity in ~ 80% yield (Scheme 1). The most satisfactory results were achieved when silver triflate was used as a catalyst, in the presence of *sym*-collidine in dichloromethane at −78°C [15]. The stereochemical outcome of the condensation did not depend on whether a pure β anomer **3–5**, or a mixture of both anomers, was employed. This can be explained in terms of kinetic control, following a fast anomerisation process. The effect of the bulky phthalimido group is clear in the light of the formation of the α,β- and α,α-disaccharides [**10a** (38%) and **10b** (29%), respectively] when **2** was condensed with 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (**9**) (Scheme 1). Similarly, reaction of **2** with 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose (**11**) at −30°C led to a mixture of **12a** (α,α; 21%) and **12b** (β,α; 7%) (Scheme 1).

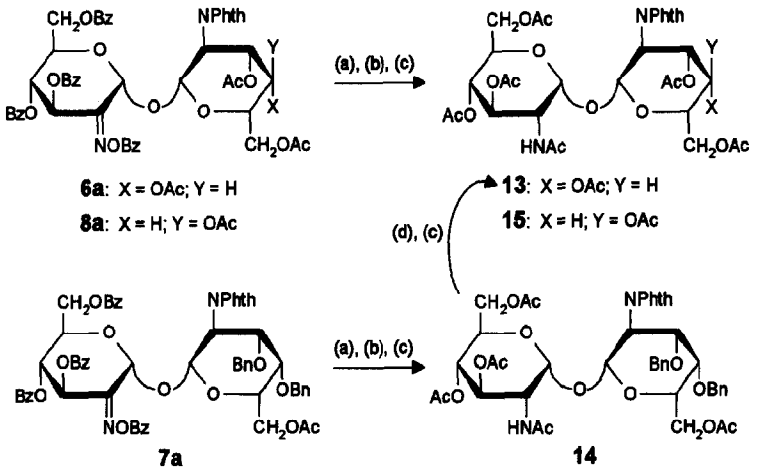
The configuration of the newly created glycosidic linkages of all the disaccharides can readily be determined by their ^{1}H NMR spectra. Thus, the β configuration of the 2-deoxy-2-phthalimido-D-*galacto* and -D-*gluco* moieties in **6–8** was



Scheme 1.

deduced from the $J_{1,2}$ values (8.0–8.9 Hz). Assignment of the α configuration to the 2-(benzoyloxyimino)-D-*arabino*-hexopyranosyl residues in **6a–8a**, **10a**, **10b**, and **12a** was made from the values $J_{3',4'}$ and $J_{4',5'}$ (both ~ 10 Hz), which are in sharp contrast with the "abnormal" values $J_{3',4'}$ (3.2 Hz) and $J_{4',5'}$ (5.6 Hz) characteristic of the β anomers **6b–8b** and **12b**. These data are in full accord with the previous observations of Lichtenthaler et al. [16], who first reported similar values for 2-(benzoyloxyimino)-α- and -β-D-*arabino*-hexopyranosides. The unusually small value of $J_{3',4'}$ in the β anomers has been explained [16] by the distortion of the $^4C_1$ conformation due to the steric congestion around the anomeric center. The assignment of α,β and β,β configurations was further supported by the positive optical rotation in the first case, and the negative rotation in the second. In the light of the above reasoning, the α,α configuration (compounds **10b** and **12a**), as well as β,α (compound **12b**) was clearly established.

Reductive amination of the oxyimino function of all the compounds reported herein required the elaboration of a special method due to the presence of the readily reducible phthalimido carbonyl groups. These were affected by B_2H_6 in THF, in Me_2S, or in Py, by $NiCl_2$–$NaBH_4$, etc., the reagents normally used for the reduction of C=N–OR [16], whereas H_2/Pd–C reduction was not stereoselective and led to a mixture of products. One of the ways we explored, which aimed at overcoming this difficulty, made use of the new $LiBH_4$–Me_3SiCl–THF species [18]. On treatment of **6a–8a** with this reagent, the oxyimino function was converted into the amino group, to afford the glucosamine unit with complete stereoselectivity, i.e., by attack from the opposite side to the anomeric moiety [16] (Scheme 2). This method, first applied by us for the reduction of the 2-oxyimino grouping in various glycosides [15,19], left the phthalimido function intact. In contrast, the



Scheme 2.

benzoyloxy blocking residues, especially those at C-3′ and C-4′, were relatively labile under the conditions used, so, for simplicity, all reduction products were immediately subjected to hydrolysis, followed by acetylation, to give the disaccharides **13–15** in good yields.

The structures of **13–15** were confirmed by their ^{1}H NMR spectra. The values of all coupling constants in both molecules, especially those of $J_{1',2'}$ (3.8 Hz) and $J_{1,2}$ (8.6–8.7 Hz), demonstrate their α,β configuration. The chemical shift of HNAc in compounds **13**, **14**, and **15** of rather unusual value (δ 1.34, 1.42, 1.46) seems to be influenced by shielding by the 2-phthalimido group of one sugar unit on the 2′-NHAc group of the second one. On the other hand, the value δ 1.54 for HNAc in **12b**, possessing the β,α configuration, suggests a similar influence of the 2′-(benzoyloxyimino) grouping.

3. Experimental

General methods.—Optical rotations were determined with a Jasco DIP-360 digital polarimeter on solutions in $CHCl_3$. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AM-500 (500 MHz) spectrometer for solutions in $CDCl_3$ (internal Me_4Si). High resolution mass spectra (HR-MS) were measured with an AMD-604 mass spectrometer. Melting points were measured on a Kofler hot-stage and are uncorrected. Reactions were monitored by TLC on Silica Gel 60 F_{254} plates (Merck), and column chromatography was performed on Silica Gel G (Merck 230–400 mesh).

In all glycosylation reactions, freshly prepared silver triflate was used; its preparation was performed as follows: to a mixture of Ag_2O (5.8 g, 25.0 mmol) and Et_2O (40 mL) in a light-protected flask was added trifluoromethanesulfonic acid (2 mL, 22.7 mmol) at −10°C. The ice bath was removed and the mixture was stirred for 1.5 h, whereupon acetone (50 mL) was added, and the mixture filtered through Celite. Solvents were removed under reduced pressure. Silver triflate thus obtained (5.6 g) was dried under reduced pressure over P_2O_5 at 60°C.

1,6-Di-O-acetyl-3,4-di-O-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranose.—To a solution of 1,6-anhydro-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranose [20] (1.44 g, 3.06 mmol) in Ac_2O (10 mL) was added CF_3CO_2H (0.5 mL). The mixture was stirred for 3 days, whereupon solid $NaHCO_3$ was added, and the mixture co-evaporated with toluene (3 × 50 mL), redissolved in toluene (50 mL), filtered through Celite, then evaporated. The yellow residue was filtered through Celite and crystallized from Et_2O to give the pure diacetate (1.66 g, 95%); mp 118–119°C; $[\alpha]_D^{20}$ + 59.9° (*c* 0.2); ^{1}H NMR: δ 1.96, 2.00 (2 s × 3 H, 2 OAc), 3.88 (dt, 1 H, H-5), 3.97 (bd, 1 H, H-4), 4.16 (dd, 1 H, H-6a), 4.22 (dd, 1 H, H-6b); 4.50 (dd, 1 H, H-3), 4.84 (dd, 1 H, H-2), 6.28 (d, 1 H, H-1), 7.02–7.10, 7.28–7.37, 7.69–7.85 (3 m, 14 H, arom.); $J_{1,2}$ 8.9, $J_{2,3}$ 11.1, $J_{3,4}$ 2.7, $J_{5,4}$ 1.0, $J_{6a,5}$ 5.8, $J_{6b,5}$ 6.7, $J_{6a,6b}$ 11.3 Hz. Anal. Calcd for $C_{32}H_{31}NO_9$ (573.60): C, 67.01; H, 5.45; N, 2.44. Found: C, 66.82; H, 5.34; N, 2.75.

3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranose (**3**).—Prepared according to the modified procedure for regioselective removal of a 1-OAc group [21]. To 20 mL of dry THF was added NaOMe (120 mg, 2.2 mmol). The mixture was stirred for 2 h and cooled to −20°C. To this suspension was added a solution of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-D-galactopyranose [22] (477 mg, 1 mmol) in THF (1 mL). The mixture was stirred at the ambient temperature. After appearance of more polar products (TLC, 1:1 hexane–EtOAc; 0.5 h), the reaction was quenched with AcOH (~ 200 μL). The mixture was washed with satd aq $NaHCO_3$ and water, then dried ($MgSO_4$), and concentrated in vacuo. Column chromatography (3:1 hexane–EtOAc) of the residue yielded **3** (205 mg, 47%) and the substrate (58 mg, 12%). Crystallization from hexane–EtOAc gave the pure β anomer; mp 153–154°C; $[\alpha]_D^{20}$ +27.1° (*c* 0.6); ^{1}H NMR: δ 1.86, 2.07, 2.20 (3 s × 3 H, 3 OAc), 3.59 (br signal, 1 H, OH), 4.13–4.23 (m, 3 H, H-5,6a,6b), 4.49 (dd, 1 H, H-2); 4.49–5.53 (m, 2 H, H-1,4), 5.89 (dd, 1 H, H-3), 7.7–7.9 (m, 4 H, NPhth); $J_{2,1}$ 8.4, $J_{2,3}$ 11.5, $J_{3,4}$ 3.4 Hz.

6-O-Acetyl-3,4-di-O-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranose (**4**).—1-*O*-Deacetylation of 1,6-di-*O*-acetyl-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranose (574 mg, 1 mmol) was performed as described for **3**. Fractionation of the reaction mixture, using 3:1 hexane–EtOAc as eluant, gave **4** (303 mg, 54%); mp 137–139°C (from toluene); $[\alpha]_D^{20}$ +67.6° (*c* 3.4); ^{1}H NMR: δ 2.02 (s, 3 H, OAc); 3.12 (d, 1 H, OH), 3.80 (bt, 1 H, H-5, 3.94 (dd, 1 H, H-4), 4.18 (dd, 1 H, H-6a); 4.24 (dd, 1 H, H-6b), 4.40 and 4.66 (AB, 2 H, OCH_2Ph), 4.47 (dd, 1 H, H-3), 4.61 (t, 1 H, H-2), 4.62 and 5.00 (AB, 2 H, OCH_2Ph), 5.24 (dd, 1 H, H-1), 7.0–7.9 (m, 14 H, arom.); $J_{1,2}$ 8.7, $J_{1,OH}$ 9.6, $J_{2,3}$ 11.1, $J_{3,4}$ 2.7, $J_{4,5}$ 0.7, $J_{6a,5}$ 5.5, $J_{6b,5}$ 6.8, $J_{6a,6b}$ 11.3 Hz. Anal. Calcd for $C_{30}H_{29}NO_8$ (531.56): C, 67.79; H, 5.50; N, 2.64. Found: C, 67.62; H, 5.45; N, 2.62.

3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl 3,4,6-tri-O-benzoyl-2-(benzoyloxyimino)-2-deoxy-α- and -β-D-arabino-hexopyranoside (**6a** *and* **6b**).—A solution of **3** (300 mg, 0.69 mmol; β:α ~ 4:1), silver triflate (300 mg, 1.17 mmol), and *sym*-collidine (83.5 mg, 92 μL, 0.69 mmol) in dry CH_2Cl_2 (10 mL), containing 3A molecular sieves (~ 150 mg), was stirred at room temperature for 1.5 h under Ar in a light-protected flask, whereupon the mixture was cooled to −78°C and the solution of bromide **2** [23] (560 mg, 0.83 mmol) in CH_2Cl_2 (2 mL) was added dropwise. Stirring at −78°C was continued for 1.5 h, then the mixture was diluted with CH_2Cl_2 (20 mL) and filtered through Celite. The filtrate was successively washed with water, aq $Na_2S_2O_3$, water, 0.1 M HCl, water, and aq $NaHCO_3$, and dried over $MgSO_4$. Evaporation of the solvent left a syrup which was passed through a silica gel column with 6:1 toluene–EtOAc as eluant. Final separation on HPLC (6:1 toluene–EtOAc) afforded pure **6a** (510 mg, 72%) as the first fraction and **6b** (13 mg, 2%) as the second.

6a: Amorphous powder; $[\alpha]_D^{20}$ + 28.1° (*c* 1.4); ^{1}H NMR: δ 1.85, 2.12, 2.28 (3 s × 3 H, 3 OAc), 4.11 (dd, 1 H, H-6a), 4.22 (dt, 1 H, H-5), 4.33 (dd, 1 H, H-6b), 4.40 (dd, 1 H, H-6′a), 4.73 (dd, 1 H, H-2), 4.76 (dd, 1 H, H-6′b), 4.85 (dt, 1 H, H-5′), 5.64 (dd, 1 H, H-4), 5.74 (dd, 1 H, H-3), 5.90 (d, 1 H, H-1), 5.99 (t, 1 H, H-4′), 6.39 (d, 1 H, H-3′), 6.46 (s, 1 H, H-1′), 7.3–8.1 (m, 24 H, arom.); $J_{1,2}$ 8.6, $J_{2,3}$

11.5, $J_{3,4}$ 3.3, $J_{4,5}$ 0.8, $J_{6a,5}$ 6.9, $J_{6b,5}$ 5.5, $J_{6a,6b}$ 11.3, $J_{3',4'}$ 10.2, $J_{4',5'}$ 10.3, $J_{6'a,5'}$ 2.7, $J_{6'b,5'}$ 2.8, $J_{6'a,6'b}$ 12.6 Hz; ^{13}C NMR: δ 20.44, 20.51, 20.74 (3 CH_3 of OAc), 51.12 (C-2), 61.53, 62.00 (C-6,6'), 66.92, 68.12, 69.26, 69.47, 69.86, 72.15 (C-3,4,5,3',4',5'), 92.93 (C-1'), 99.80 (C-1), 154.93 (C-2'), 161.79, 164.72, 165.02, 166.13 (4 C=O of OBz), 167.11, 168.44 (2 C=O of NPhth); 169.72, 170.21, 170.62 (3 C=O of OAc). Anal. Calcd for $C_{54}H_{46}N_2O_{19}$ (1026.96): C, 63.16; H, 4.51; N, 2.73. Found: C, 63.08; H, 4.25; N, 2.77.

6b: Amorphous powder; $[\alpha]_D^{20}$ −16.2° (*c* 1.1); ^{1}H NMR: δ 1.85, 2.01, 2.12 (3 s × 3 H, 3 OAc), 4.09–4.21 (m, 5 H, H-5,6a,5',6'a,6'b), 4.32 (dd, 1 H, H-6b), 4.71 (dd, 1 H, H-2), 5.48–5.53 (m, 2 H, H-4,4'), 5.88 (dd, 1 H, H-3), 5.97 (d, 1 H, H-3'), 6.05 (d, 1 H, H-1), 6.40 (s, 1 H, H-1'), 7.2–8.2 (m, 24 H, arom.); $J_{1,2}$ 8.5, $J_{2,3}$ 11.2, $J_{3,4}$ 3.2, $J_{6b,5}$ 5.6, $J_{6b,6a}$ 11.5, $J_{3',4'}$ 3.0 Hz. Anal. Calcd for $C_{54}H_{46}N_2O_{19}$ (1026.96): C, 63.16; H, 4.51; N, 2.73. Found: C, 63.12; H, 4.51; N, 2.75.

*6-O-Acetyl-3,4-di-O-benzyl-2-deoxy-2-phthalimido-β-*D*-galactopyranosyl 3,4,6-tri-O-benzoyl-2-(benzoyloxyimino)-2-deoxy-α- and -β-*D*-*arabino*-hexopyranoside* (**7a** *and* **7b**).—A solution of **4** (500 mg, 0.942 mmol; $\beta:\alpha \sim 2.5:1$) in CH_2Cl_2 (10 mL) containing 3A molecular sieves (~ 200 mg) and *sym*-collidine (116 mg, 127 μL, 0.959 mmol) was treated with bromide **2** (735 mg, 1.094 mmol) according to the procedure described for **6a**. Isolation of the product mixture as described for **6a**, followed by HPLC chromatography using 10:1 toluene–EtOAc as eluant, gave **7a** (820 mg, 77%) as the first and **7b** (28 mg, 3%) as the second fraction.

7a: Mp 98–100°C (from Et_2O); $[\alpha]_D^{25}$ +78.1° (*c* 1.5); ^{1}H NMR: δ 2.08 (s, 3 H, OAc); 3.88 (ddd, 1 H, H-5), 3.99 (dd, 1 H, H-4), 4.18 (dd, 1 H, H-6a), 4.25–4.35 (m, 3 H, H-3, 6b, 6'a), 4.36 and 4.65 (AB, 2 H, OCH_2Ph), 4.67 and 5.07 (AB, 2 H, OCH_2Ph), 4.76 (dd, 1 H, H-6'b), 4.89–4.94 (m, 2 H, H-2,5'), 5.71 (d, 1 H, H-1), 6.00 (t, 1 H, H-4'), 6.35 (d, 1 H, H-3), 6.40 (s, 1 H, H-1'), 7.0–7.1 and 7.3–8.1 (2 m, 34 H, arom.); $J_{1,2}$ 8.7, $J_{4,3}$ 2.7, $J_{4,5}$ 0.9, $J_{5,6a}$ 4.3, $J_{5,6b}$ 7.3, $J_{6a,6b}$ 11.7, $J_{3',4'}$ 10.0, $J_{4',5'}$ 10.1, $J_{6'b,5'}$ 2.5, $J_{6'b,6'a}$ 12.5 Hz; ^{13}C NMR: δ 20.84 (CH_3 of OAc), 52.48 (C-2), 61.57, 63.99 (C-6,6'), 68.89, 69.64, 69.92, 72.19, 73.92, 74.75 (C-3,4,5,3',4',5'), 92.67 (C-1'), 100.08 (C-1), 155.32 (C-2'), 161.81, 164.72, 164.86, 166.14 (4 C=O of OBz), 170.91 (C=O of OAc). Anal. Calcd for $C_{64}H_{54}N_2O_{17}$ (1123.14): C, 68.44; H, 4.85; N, 2.49. Found: C, 68.49; H, 4.57; N, 2.70.

7b: Amorphous powder; $[\alpha]_D^{25}$ −68.0° (*c* 0.5); ^{1}H NMR: δ 1.94 (s, 3 H, OAc), 3.84 (bt, 1 H, H-5), 3.99 (bd, 1 H, H-4), 4.07–4.15 (m, 2 H, H-5',6'a), 4.20 (dd, 1 H, H-6'b), 4.27 (dd, 1 H, H-6a), 4.33 (dd, 1 H, H-6b), 4.36 and 4.66 (AB, 2 H, OCH_2Ph), 4.45 (dd, 1 H, H-3), 4.63 and 5.04 (AB, 2 H, OCH_2Ph), 4.91 (dd, 1 H, H-2), 5.56 (dd, 1 H, H-4'), 5.80 (d, 1 H, H-1), 6.03 (d, 1 H, H-3'), 6.41 (s, 1 H, H-1'), 6.99–8.07 (m, 34 H, arom.); $J_{1,2}$ 8.6, $J_{2,3}$ 11.0, $J_{3,4}$ 2.7, $J_{4,5} < 0.8$, $J_{5,6a}$ 6.0, $J_{5,6b}$ 6.5, $J_{6a,6b}$ 11.4, $J_{3',4'}$ 3.3, $J_{4',5'}$ 5.4, $J_{6'b,5'}$ 6.7, $J_{6'b,6'a}$ 11.0 Hz; ^{13}C NMR: δ 20.69 (CH_3 of OAc), 52.68 (C-2), 62.74, 63.66 (C-6,6'), 69.19, 69.40, 72.02, 72.27, 73.07, 74.67 (C-3,4,5,3',4',5'), 89.73 (C-1'), 96.12 (C-1), 154.70 (C-2), 162.87, 164.55, 164.58, 165.35 (4 C=O of OBz), 170.43 (C=O of OAc). Anal. Calcd for $C_{64}H_{54}N_2O_{17}$ (1123.14): C, 68.44; H, 4.85; N, 2.49. Found: C, 68.95; H, 4.55; N, 2.55.

*3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl 3,4,6-tri-O-benzoyl-2-(benzoyloxyimino)-2-deoxy-α- and -β-*D*-arabino-hexopyranoside* (**8a** *and* **8b**).—A

solution of **5** (225 mg, 0.517 mmol; $\beta:\alpha \sim 5:1$) and silver triflate (225 mg, 0.875 mmol) in CH_2Cl_2 (10 mL) containing 3A molecular sieves (~ 150 mg) and *sym*-collidine (62.6 mg, 69 μL, 0.526 mmol) was treated with bromide **2** (450 mg, 0.670 mmol) according to the procedure described for **6a**. Separation of the reaction products as described for **6a** gave **8a** (423 mg, 80%) and **8b** (11 mg, 2%).

8a: (First fraction); amorphous powder; $[\alpha]_D^{20}$ +45.5° (*c* 3.1); ^{1}H NMR: δ 1.86, 2.06, 2.16 (3 s × 3 H, 3 OAc), 4.00 (ddd, 1 H, H-5), 4.20 (dd, 1 H, H-6a), 4.35 (dd, 1 H, H-6b), 4.42 (dd, 1 H, H-6′a), 4.48 (dd, 1 H, H-2), 4.76–4.84 (m, 2 H, H-5′, 6′b), 5.20 (t, 1 H, H-4), 5.73 (dd, 1 H, H-3), 5.99 (d, 1 H, H-1), 6.00 (t, 1 H, H-4′), 6.38 (d, 1 H, H-3′), 6.47 (s, 1 H, H-1′), 7.3–8.1 (m, 24 H, arom.); $J_{1,2}$ 8.9, $J_{2,3}$ 10.7, $J_{3,4}$ 9.3, $J_{4,5}$ 9.8, $J_{5,6a}$ 1.7, $J_{5,6b}$ 5.35, $J_{6a,6b}$ 12.4, $J_{3',4'}$ 10.0, $J_{4',5'}$ 10.3, $J_{6'a,5'}$ 2.7, $J_{6'a,6'b}$ 12.4 Hz; ^{13}C NMR: δ 20.37, 20.62, 20.81 (3 CH_3 of OAc), 54.44 (C-2), 61.60, 62.05 (C-6,6′), 68.60, 69.29, 69.56, 69.96, 70.80, 73.32 (C-3,4,5,3′,4′,5′), 92.94 (C-1′), 99.24 (C-1), 154.88 (C-2′), 161,88, 164.76, 165.05, 166.13 (4 C=O of OBz), 169.45, 170.08, 170.67 (3 C=O of OAc). Anal. Calcd for $C_{54}H_{46}N_2O_{19}$ (1026.96): C, 63.16; H, 4.51; N, 2.73. Found: C, 63.30; H, 4.35; N, 2.75.

8b: (Second fraction); amorphous powder; $[\alpha]_D^{20}$ −44.1° (*c* 1.7); ^{1}H NMR: δ 1.85, 1.94, 2.02 (3 s × 3 H, 3 OAc), 3.86 (dd, 1 H, H-6a), 3.90 (ddd, 1 H, H-5), 4.13 (q, 1 H, H-5′), 4.19 (dd, 1 H, H-6b), 4.24 (dd, 1 H, H-6′a), 4.34 (dd, 1 H, H-6′b), 4.50 (dd, 1 H, H-2), 5.12 (dd, 1 H, H-4′), 5.55 (dd, 1 H, H-4), 5.85 (dd, 1 H, H-3′), 6.02 (d, 1 H, H-1), 6.07 (d, 1 H, H-3′), 7.2–8.2 (m, 24 H, arom.); $J_{1,2}$ 8.5, $J_{2,3}$ 10.6, $J_{3,4}$ 9.2, $J_{4,5}$ 10.0, $J_{6a,5}$ 2.4, $J_{6b,5}$ 4.6, $J_{6a,6b}$ 12.2, $J_{3',4'}$ 3.2, $J_{4',5'}$ 5.6, $J_{6'a,5'}$ 6.0, $J_{6'a,6'b}$ 11.5, $J_{6'b,5'}$ 5.9 Hz; ^{13}C NMR: δ 20.37, 20.45, 20.58 (3 CH_3 of OAc), 54.70 (C-2), 61.84, 63.77 (C-6,6′), 68.72, 69.42, 69.46, 70.62, 72.47, 72.64 (C-3,4,5,3′,4′,5′), 90.61 (C-1′), 96.29 (C-1), 155.04 (C-2′), 162.60, 164.47, 164.64, 165.43 (4 C=O of OBz), 169.42, 170.06, 170.59 (3 C=O of OAc). Anal. Calcd for $C_{54}H_{46}N_2O_{19}$ (1026.96): C, 63.16; H, 4.51; N, 2.73. Found: C, 62.76; H, 4.35; N, 2.71.

*2,3,4,6-Tetra-*O*-acetyl-β- and -α-*D*-glucopyranosyl 3,4,6-tri-*O*-benzoyl-2-(benzoyloxyimino)-2-deoxy-α4l-*D*-arabino-hexopyranoside* (**10a** *and* **10b**).—A solution of **9** [24] {108 mg, 0.310 mmol; pure β anomer, $[\alpha]_D^{20}$ +4.5° (*c* 1.3)}, silver triflate (167 mg, 0.650 mmol), and *sym*-collidine (42 μL, 0.316 mmol) in CH_2Cl_2, containing 3A molecular sieves (~ 100 mg), was treated with bromide **2** (265 mg, 0.394 mmol) according to the procedure described for **6a**. Separation of the reaction products, as described for **6a** (6:1 toluene–EtOAc), gave **10a** (110 mg, (38%) and **10b** (85 mg, 29%).

10a: (First fraction); amorphous powder; $[\alpha]_D^{20}$ +48.7° (*c* 0.8); ^{1}H NMR: δ 1.88, 2.02, 2.04, 2.11 (4 s × 3 H, 4 OAc), 3.78 (m, 1 H, H-5), 4.15 (dd, 1 H, H-6a), 4.23 (dd, 1 H, H-6b), 4.42 (dd, 1 H, H-6′a), 4.73–4.84 (m, 2 H, H-5′,6′b), 4.97 (d, 1 H, H-1), 5.10 (t, 1 H, H-2), 5.12 (t, 1 H, H-4), 5.27 (t, 1 H, H-3), 6.05 (t, 1 H, H-4′), 6.37 (d, 1 H, H-3′), 6.46 (s, 1 H, H-1), 7.29–7.67, 7.95–8.11 (2 m, 20 H, arom.); $J_{1,2}$ 8.0, $J_{2,3}$ 9.7, $J_{3,4}$ 9.8, $J_{4,5}$ 9.5, $J_{5,6a}$ 2.2, $J_{5,6b}$ 5.0, $J_{6a,6b}$ 12.5, $J_{3',4'}$ 10.0, $J_{4',5'}$ 10.1, $J_{5',6'a}$ 3.3, $J_{6'a,6'b}$ 12.9 Hz. Anal. Calcd for $C_{48}H_{45}NO_{19}$ (939.88): C, 61.34; H, 4.83; N, 1.49. Found: C, 61.40; H, 4.59, N, 1.37.

10b: (Second fraction); amorphous powder; $[\alpha]_D^{20}$ +127.6° (*c* 1.0); ^{1}H NMR: δ 1.96, 2.03, 2.04, 2.09 (4 s × 3 H, 4 OAc); 3.86 (dd, 1 H, H-6a), 4.04 (dd, 1 H, H-6b),

4.11 (dt, 1 H, H-5), 4.48 (dd, 1 H, H-6'a), 4.62 (dd, 1 H, H-6'b), 4.66 (m, H-1, H-5'), 5.14 (dd, 1 H, H-2), 5.18 (t, 1 H, H-4), 5.55 (dd and d, 2 H, H-1,3), 5.97 (t, 1 H, H-4'), 6.45 (d, 1 H, H-3'), 6.51 (s, 1 H, H-1'), 7.38–7.64, 7.95–8.10 (2 m, 20 H, arom.); $J_{2,1}$ 3.8, $J_{2,3}$ 10.3, $J_{4,3} = J_{4,5} = 9.7$, $J_{6a,5}$ 2.0, $J_{6b,5}$ 2.9, $J_{6a,6b}$ 12.6, $J_{4',3'} = J_{4',5'} = 9.9$, $J_{6'a,5'}$ 5.1, $J_{6'b,5'}$ 3.5, $J_{6'a,6'b}$ 12.2 Hz. Anal. Calcd for $C_{48}H_{45}NO_{19}$ (939.88): C, 61.34; H, 4.83; N, 1.49. Found: C, 61.10; H, 4.71; N, 1.65.

*2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-glucopyranosyl 3,4,6-tri-*O*-benzoyl-2-(benzoyloxyimino)-2-deoxy-α- and -β-*D*-arabino-hexopyranoside* (**12a** *and* **12b**).—A solution of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose (**11**) [25] {174 mg, 0.500 mmol; pure α anomer, $[\alpha]_D^{20}$ +46.5° (*c* 1.0) (lit. [25] $[\alpha]_D^{15}$ +46°)} and silver triflate (220 mg, 0.856 mmol) in CH_2Cl_2 (10 mL) containing 3A molecular sieves (~ 100 mg) and *sym*-collidine (67 μL, 0.504 mmol) was treated at −30°C with bromide **2** (437 mg, 0.650 mmol) according to the procedure described for **6a**. Separation of the reaction mixture, as described for **6a** (2:1 toluene–EtOAc) gave **12a** (97 mg, 21%) and **12b** (35 mg, 7%).

12a: (First fraction); amorphous powder; $[\alpha]_D^{20}$ +97.3° (*c* 1.4); ^{1}H NMR: δ 1.96, 2.00, 2.02, 2.08 (4 s × 3 H, 3 OAc and NAc), 3.85 (dd, 1 H, H-6a), 3.97–4.03 (m, 2 H, H-5,6b), 4.44 (ddd, 1 H, H-2), 4.52 (dd, 1 H, H-6'a), 4.60 (dd, 1 H, H-6'b), 4.64 (ddd, 1 H, H-5'), 5.23 (t, 1 H, H-4), 5.31 (dd, 1 H, H-3), 5.47 (d, 1 H, H-1), 5.87 (t, 1 H, H-4'), 6.40 (d, 1 H, NH); 6.50 (s, 1 H, H-1'), 6.51 (d, 1 H, H-3'), 7.95–8.01, 8.04–8.08 (2 m, 20 H, arom.); $J_{1,2}$ 3.8, $J_{2,3}$ 10.9, $J_{3,4}$ 9.6, $J_{4,5}$ 9.6, $J_{6a,5}$ 3.3, $J_{6a,6b}$ 13.7, $J_{4',3'} = J_{4',5'} = 10.0$, $J_{6'a,5'}$ 5.1, $J_{6'a,6'b}$ 12.3, $J_{6'b,5}$ 5.1, $J_{2,NH}$ 8.7 Hz. Anal. Calcd for $C_{48}H_{46}N_2O_{18}$ (938.90): C, 61.40; H, 4.94; N, 2.98; Found: C, 61.00; H, 4.89; N, 3.17.

12b: (Second fraction); amorphous powder; $[\alpha]_D^{20}$ +37.2° (*c* 0.5); ^{1}H NMR: δ 1.54, 1.91, 1.97, 2.05 (4 s × 3 H, 3 OAc and NAc), 3.97 (dd, 1 H, H-6a), 4.12 (dd, 1 H, H-6b), 4.16 (ddd, 1 H, H-5'), 4.27 (ddd, 1 H, H-5), 4.37 (ddd, 1 H, H-2), 4.68 (dd, 1 H, H-6'a), 4.84 (dd, 1 H, H-6'b), 5.10 (t, 1 H, H-4), 5.18 (dd, 1 H, H-3), 5.50 (d, 1 H, H-1), 5.65 (d, 1 H, NH), 5.82 (dd, 1 H, H-4'), 6.15 (d, 1 H, H-3'), 6.22 (s, 1 H, H-1'), 7.4–8.1 (m, 20 H, arom.); $J_{1,2}$ 3.6, $J_{2,3}$ 10.7, $J_{3,4}$ 9.5, $J_{5,4}$ 10.2, $J_{5,6a}$ 2.3, $J_{5,6b}$ 3.5, $J_{6a,6b}$ 12.6, $J_{3',4'}$ 2.2, $J_{4',5'}$ 7.0, $J_{5',6'a}$ 3.8, $J_{5',6'b}$ 5.8, $J_{6'a,6'b}$ 12.0, $J_{2,NH}$ 9.5 Hz. Anal. Calcd for $C_{48}H_{46}N_2O_{18}$ (938.90): C, 61.40; H, 4.94; N, 2.98; Found: C, 61.12; H, 4.70; N, 3.04.

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-*D*-galactopyranosyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-glucopyranoside* (**13**).—*Method A*. To a solution of $LiBH_4$ (1.17 mmol) in anhyd THF (5 mL) was added Me_3SiCl (2.34 mmol) dropwise at room temperature under Ar. After 1 h, the mixture was cooled to −20°C and a solution of **6a** (240 mg, 0.23 mmol) in THF (2 mL) was slowly added, whereupon the mixture was allowed to reach room temperature. After 3 h, the mixture was heated to 40°C for 1 h and then cooled to 0°C, MeOH was added dropwise until the bubbling subsided, and the solution was neutralized with solid $NaHCO_3$ and filtered through Celite. The filtrate was co-evaporated in vacuo with toluene, dry K_2CO_3 was added to the residue dissolved in abs. MeOH, and the mixture was stirred overnight. After filtration through Celite, the solvent was removed under reduced pressure and the residue was acetylated with Ac_2O (2 mL) in pyridine

(5 mL). Reagents were evaporated in vacuo with toluene, and the residue was chromatographed on a silica gel column with 4:1 toluene–acetone as eluant to give pure **13** (80 mg, 44%); mp 113–116°C; $[\alpha]_D^{20}$ +62.6° (*c* 0.5); ^{1}H NMR: δ 1.46, 1.87, 1.98, 2.03, 2.09, 2.09, 2.27 (7 s × 3 H, 6 OAc and NAc), 4.03–4.09 (m, 2 H, H-6a,6b), 4.13 (bt, 1 H, H-5), 4.21–4.28 (m, 3 H, H-2′,6′a,6′b), 4.31 (dt, 1 H, H-5′), 4.57 (dd, 1 H, H-2), 4.87 (d, 1 H, H-1), 5.17 and 5.23 (2 t, 2 × 1 H, H-3′,4′), 5.42 (d, 1 H, NH), 5.44 (d, 1 H, H-1), 5.50 (bd, 1 H, H-4), 5.88 (dd, 1 H, H-3), 7.75–7.89 (m, 4 H, NPhth), $J_{1,2}$ 8.6, $J_{2,3}$ 11.5, $J_{3,4}$ 3.4, $J_{4,5}$ 0.6, $J_{5,6a} \approx J_{5,6b} \approx 5.5$, $J_{1',2'}$ 3.8, $J_{3',2'} = J_{3',4'} = 9.6$, $J_{4',5'}$ 9.7, $J_{5',6'a} \approx J_{5',6'b} \approx 2.6$, $J_{NH,2'}$ 9.5 Hz; ^{13}C NMR: δ 20.74, 20.59, 20.65, 20.66, 20.68, 20.73, 22.32 (7 CH_3 of OAc), 51.44, 51.56 (C-2,2′), 61.31, 62.03 (C-6,6′), 66.62, 67.50, 67.61, 68.51, 71.30, 71.60 (C-3,4,5,3′,4′,5′), 97.94 (C-1′), 98.93 (C-1), 123.56, 124.32, 128.25, 129.06, 134.66, 135.05 (6 C arom. of NPhth), 167.87, 168.02 (2 C=O of NPhth), 169.18, 169.60, 169.62, 170.19, 170.50, 170.74, 171.30 (7 C=O of OAc). Anal. Calcd for $C_{34}H_{40}N_2O_{18}$ (764.69): C, 53.40; H, 5.27; N, 3.66. Found: C, 53.29; H, 5.48; N, 3.40.

Method B. A solution of **14** (36 mg, 41.8 μmol) in EtOH was hydrogenated in the presence of Pd–C (10%) as a catalyst. After 16 h, the mixture was filtered through Celite and concentrated to dryness. The residue was acetylated with Ac_2O in pyridine for 3 h. Excess of the reagents were co-evaporated in vacuo with toluene. Column chromatography of the residue with 1:1 → 1:2 hexane–EtOAc as eluant gave **13** (27 mg, 84%), identical by ^{1}H NMR with the product described under *A*.

6-O-Acetyl-3,4-di-O-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-glucopyranoside (**14**).—Compound **7** (152 mg, 0.135 mmol) was reduced, according to the procedure (*A*) described for **13**, to give **14** (57 mg, 49%); amorphous powder; $[\alpha]_D^{20}$ +57.4° (*c* 1.2); ^{1}H NMR: δ 1.42, 1.95, 2.00, 2.03, 2.06 (5 s × 3 H, 4 OAc and NAc), 3.77 (m, 1 H, H-5), 3.95 (dd, 1 H, H-4), 4.05 (dd, 1 H, H-6a), 4.11 (dd, 1 H, H-6′a), 4.17–4.22 (m, 3 H, H-2′,6b,6′b), 4.34 and 4.66 (AB, 2 H, OCH_2Ph), 4.36 (dt, 1 H, H-5′), 4.42 (dd, 1 H, H-3), 4.66 and 5.02 (AB, 2 H, OCH_2Ph), 4.73 (dd, 1 H, H-2), 4.80 (d, 1 H, H-1′), 5.14 and 5.20 (2 t, 2 × 1 H, H-3′,4′), 5.24 (d, 1 H, H-1), 5.46 (d, 1 H, NH), 6.99–7.10, 7.31–7.41, 7.70–7.85 (3 m, 14 H, arom.); $J_{1,2}$ 8.7, $J_{2,3}$ 11.2, $J_{3,4}$ 2.8, $J_{4,5}$ 0.8, $J_{5,6a}$ 7.1, $J_{5,6b}$ 4.7, $J_{6a,6b}$ 11.5, $J_{1',2'}$ 3.8, $J_{3',2'} = J_{3',4'} = J_{4',5'} = 9.3$, $J_{5',6'a} \approx J_{5',6'b} \approx 2.3$, $J_{6'a,6'b}$ 12.5, $J_{NH,2'}$ 9.6 Hz. HR-MS: Calcd for $C_{44}H_{48}N_2O_{16}$: 860.3010. Found: 860.3004.

3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-glucopyranoside (**15**).—Compound **8** (138 mg, 0.135 mmol) was reduced, according to the procedure (*A*) described for **13**, to give **15** (46 mg, 45%); amorphous powder; $[\alpha]_D^{20}$ +67.9° (*c* 1.4); ^{1}H NMR: δ 1.34, 1.88, 1.97, 2.03, 2.05, 2.08, 2.15 (7 s × 3 H, 6 OAc and NAc), 3.93 (ddd, 1 H, H-5), 4.07 (dd, 1 H, H-6′a), 4.17 (dd, 1 H, H-6a), 4.20-4.30 (m, 4 H, H-6b, 2′, 5′, 6′b), 4.37 (dd, 1 H, H-2′), 4.91 (d, 1 H, H-1′), 5.13 (dd, 1 H, H-4), 5.15–5.20 (m, 2 H, H-3′, 4′); 5.38 (d, 1 H, NH), 5.54 (d, 1 H, H-1′), 5.82 (dd, 1 H, H-3), 7.74–7.91 (m, 4 H, NPhth); $J_{1,2}$ 8.6, $J_{2,3}$ 10.7, $J_{3,4}$ 9.1, $J_{4,5}$ 10.2, $J_{5,6a}$ 2.1, $J_{5,6b}$ 5.3, $J_{6a,6b}$ 12.3, $J_{1',2'}$ 3.8, $J_{6'a,5}$ 3.0, $J_{6'a,6'b}$ 13.1, $J_{NH,2'}$ 9.3 Hz. Anal. Calcd for $C_{34}H_{40}N_2O_{18}$ (764.69): C, 53.40; H, 5.27; N, 3.66. Found: C, 53.23; H, 5.57; N, 3.33.

References

[1] G.G. Birch, *Adv. Carbohydr. Chem.*, 18 (1963) 201–225; A.D. Elbein, *Adv. Carbohydr. Chem. Biochem.*, 30 (1974) 227–256.
[2] G. Lemaire, J.P. Tenu, and J.-F. Petit, *Med. Res. Rev.*, 6 (1986) 243–274.
[3] S. Umezawa, *Adv. Carbohydr. Chem. Biochem.*, 30 (1974) 111–182.
[4] F. Arcamone and F. Bizioli, *Gazz. Chim. Ital.*, 87 (1957) 896–902.
[5] L.A. Dolak, T.M. Castle, and A.L. Laborde, *J. Antibiot.*, 33 (1980) 690–694.
[6] H. Naganawa, N. Usui, T. Takita, M. Hamada, K. Haeda, and H. Umezawa, *J. Antibiot.*, 27 (1974) 145–146.
[7] M. Uramoto, N. Otake, and H. Yonehara, *J. Antibiot., Ser. A*, 20 (1967) 236–237.
[8] O.L. Galmarini and V. Deulofeu, *Tetrahedron*, 15 (1961) 76–86; A.K. Ganguly and A.K. Saksena, *J. Antibiot.*, 28 (1975) 707–709; A.K. Ganguly, O.Z. Sarre, and J. Morton, *J. Chem. Soc., Chem. Commun.*, (1969) 1488–1489; W.D. Ollis, C. Smith, and D.E. Wright, *Tetrahedron*, 35 (1979) 105–127.
[9] T. Tsuno, C. Ikeda, K.-I. Numata, K. Tomita, M. Konishi, and H. Kawaguchi, *J. Antibiot.*, 39 (1986) 1001–1003.
[10] A. Takatsuki, H. Arima, and G. Tamura, *J. Antibiot.*, 24 (1971) 215–223.
[11] H. Paulsen, *Angew. Chem.*, 94 (1982) 184–201; R.R. Schmidt, *ibid.*, 98 (1986) 213–236.
[12] V.A. Oláh, J. Harangi, and A. Lipták, *Carbohydr. Res.*, 174 (1988) 113–120.
[13] T. Suami, H. Sasai, K. Matsuno, and N. Suzuki, *Carbohydr. Res.*, 143 (1985) 85–96.
[14] S. Danishefsky, S.L. DeNinno, S. Chen, L. Boisvert, and M. Barbachyn, *J. Am. Chem. Soc.*, 111 (1989) 5810–5818.
[15] W. Karpiesiuk and A. Banaszek, *J. Carbohydr. Chem.*, 9 (1990) 909–914.
[16] F.W. Lichtenthaler, E. Kaji, and S. Weprek, *J. Org. Chem.*, 50 (1985) 3505–3515; F.W. Lichtenthaler and E. Kaji, *Liebigs Ann. Chem.*, (1985) 1659–1668.
[17] A.G. Myers, D.Y. Gin, and D.H. Rogers, *J. Am. Chem. Soc.*, 115 (1993) 2036–2038.
[18] A. Giannis and S. Sandhof, *Angew. Chem. Int. Ed. Engl.*, 28 (1989) 218–220.
[19] A. Banaszek and W. Karpiesiuk, *Carbohydr. Res.*, 251 (1994) 233–242.
[20] J. Garcia, J. Vilarrasa, X. Bordas, and A. Banaszek, *Tetrahedron Lett.*, 27 (1986) 639–640.
[21] K. Watanabe, K. Itoh, Y. Takamura, and Y. Ishido, *Carbohydr. Res.*, 156 (1986) 241–246.
[22] H. Paulsen and A. Bünsch, *Carbohydr. Res.*, 100 (1982) 143–167.
[23] F.W. Lichtenthaler, P. Jarglis, and W. Hempe, *Liebigs Ann. Chem.*, (1983) 1959–1972.
[24] C.M. McCloskey and G.H. Coleman, *Org. Synth.*, Coll. Vol. 3 (1955) 434–436.
[25] K. Watanabe, K. Itoh, Y. Araki, and Y. Ishido, *Carbohydr. Res.*, 154 (1986) 165–176.