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## Note

# Synthesis of amylostatin (XG)*

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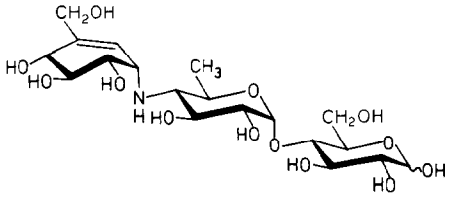
In a preceding paper[1], we described the synthesis of adiposin-1, isolated from α-D-glucoside hydrolase inhibitor, adiposin. As an extension of synthetic work on pseudo-oligosaccharides exhibiting interesting biological activity, the synthesis of amylostatin (XG) (**1**) is now reported. Compound **1** was first isolated from the hydrolyzate of an α-D-glucosidase inhibitor, amylostatin, produced by *Streptomyces diastaticus* subsp. *amylostaticus* and, later found in the fermentation broth[2]. Pseudo-trisaccharide **1** is a common core-constituent of other analogous α-D-glucosidase inhibitors: acarbose and its homologs, and trestatin[3]. The first chemical synthesis of **1** was achieved by Sakairi and Kuzuhara[4] using a coupling reaction of the protected aminodeoxydisaccharide with a protected hydroxymethyl(trihydroxy)cyclohexenyl bromide. In the present synthesis, coupling of a new dianhydro derivative (**3**) of the disaccharide with the protected DL-valienamine[5] (**6**) was undertaken to construct the pseudo-trisaccharide structure containing an imino linkage.




Amylostatin (XG) 1

Treatment of 2,3,2′,3′-tetra-*O*-acetyl-1,6-anhydro-6′-deoxy-4′-*O*-*p*-tolylsulfonyl-β-maltose[6] (**2**) with a large excess of methanolic sodium methoxide in 5:3 chloroform–methanol for 4 h at 0–5° gave, after crystallization from ethanol, a

*Synthesis of Pseudo-oligosaccharidic Glycosidase Inhibitors, Part II. For Part I, see ref. 1.
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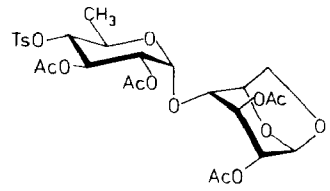
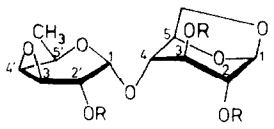


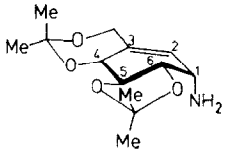
2



3 R=H

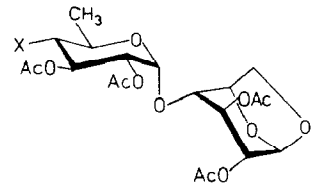
4 R=Ac

5 R=THP

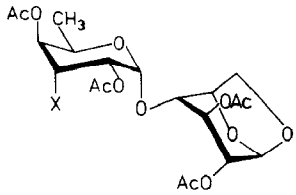


6

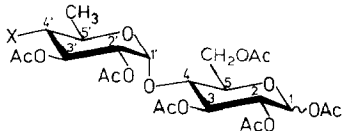
(racemate)



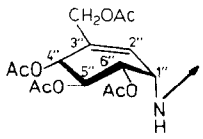
7a,b

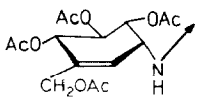


8a,b



9a,b

a X = 

b X = 

single, crystalline product, 1,6-anhydro-4-*O*-(3,4-anhydro-6-deoxy-α-D-galacto-pyranosyl)-β-D-glucopyranose (3) in 61% yield. The $^1$H-n.m.r. spectrum of **3** showed at δ 3.29 a two-proton singlet for the C-3′ and C-4′ epoxide protons, which was in accord with data for the corresponding 6′-hydroxy compound[1]. Under these conditions, the presence of an isomer formed by epoxide-group migration was not observed.

Coupling of equimolar amounts of **3** and DL-4,7:5,6-di-*O*-isopropylidene-

(*1,4,6/5*)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenylamine (**6**) was carried out in 1:8 *N,N*-dimethylformamide–2-propanol in a sealed tube for 55 h at 120°. At that time, t.l.c. indicated formation of new compounds, together with a trace of **3**. The products were isolated and then treated with acetic anhydride in pyridine overnight at room temperature. Fractionation of the resulting acetates on a column of silica gel with 1:5 butanone–toluene as eluant gave two components. The slower-moving component was treated with 70% aqueous acetic acid for 1.5 h at 55° to remove the isopropylidene groups and subsequently acetylated conventionally to give the protected pseudo-trisaccharide **8a**, $[\alpha]_D^{21}$ +22.7° ($CHCl_3$), in 24% yield. Similar treatment of the faster-moving component yielded a mixture of compounds that was separated by chromatography on silica gel. Elution with 1:2 acetone–hexane gave three protected pseudo-trisaccharides. The first fraction gave crystalline **8b**, $[\alpha]_D^{25}$ −7.5° ($CHCl_3$), in 31.8% yield. The second fraction gave the oily **7a**, $[\alpha]_D^{19}$ +52.2° ($CHCl_3$), in 6.1% yield. The third fraction gave the oily **7b**, $[\alpha]_D^{23}$ −1.6° ($CHCl_3$), in 5.7% yield. The structures of **7a, 7b, 8a,** and **8b** were tentatively assigned as shown in Scheme II on the basis of $^1$H-n.m.r. spectroscopy, in particular, by judging from the signals for protons on carbon atoms of the sugar component bonding to the imino groups. Thus, in the spectra of **7a** and **7b**, these signals appeared at $\delta$ 2.43–2.48 as wide triplets ($J$ 10 Hz), indicating that the protons were oriented axially; namely, two vicinal axial protons. In contrast, the $^1$H-n.m.r. spectra of **8a** and **8b** revealed the corresponding signals as narrow triplets ($J$ 4.5 Hz) at $\delta$ 3.03–3.16. Therefore, it was clear that two sets of compounds **7a** and **7b**, and **8a** and **8b**, were both diastereomeric pairs, and the former, the minor products, were formed by diequatorial opening of the epoxide ring of **3** and the latter arose by preferential diaxial opening. Differentiation between **7a** and **7b**, as well as between **8a** and **8b**, was made on the basis of the empirical rule of superposition of rotatory contributions by the cyclohexane parts, using a positive value of the specific rotation of (1*S*)-penta-*N,O*-acetylvalienamine {$[\alpha]_D^{23}$ +30.2° ($CHCl_3$)}[7]. The assigned structures of **7a** and **7b** were later confirmed by converting into the corresponding pseudo-trisaccharide decaacetates (**9a** and **9b**), which were compared with an authentic sample of that of amylostatin (XG). Thus, treatment of **7a** with 70:30:1 acetic acid–acetic anhydride–conc. sulfuric acid for 3 h at room temperature gave **9a**, $[\alpha]_D^{21}$ +95.4° ($CHCl_3$), in 88% yield. Its $^1$H-n.m.r. spectrum (400 MHz) in chloroform-*d* was superposable on that of an authentic sample[2,4]. Similarly, compound **7b** was transformed into **9b**, whose $^1$H-n.m.r. spectral data were essentially identical to those of **9a**, except for a small upfield shift of the signal of H-2″. Accordingly, compounds **9a** and **9b** are diastereomers.

We then attempted to protect the C-2′ hydroxyl group of **3** with the tetrahydropyranyl group, expecting to improve the yields of the products derived by nucleophilic attack at the C-4′. Treatment of **3** with a large excess of 3,4-dihydro-2*H*-pyran in dichloromethane in the presence of pyridinium *p*-toluenesulfonate gave the tetrahydropyranyl ether (**5**) in good yield. The coupling of **5** with **6** was performed in 2-propanol for 80 h at 120°, and the condensates were isolated as the

octaacetyl derivatives (**7a, 7b,** and **8b**), the yields of which were similar to those observed in the reaction of **3** with **6**. Thus, nucleophilic attack at the epoxide ring resulted in predominantly diaxial opening in both cases. It is noteworthy that the condensation of the 6′-hydroxy compound of **3** with **6** produced, unexpectedly, the diaxial and diequatorial opening products in almost equal proportion[1]. Therefore, the C-6′ hydroxyl group may be involved in stabilizing the less-favored conformation in the transition state, being favorable for the diequatorial cleavage of the epoxide ring.

## EXPERIMENTAL

*General methods.* — Melting points were determined with a Büchi 510 capillary melting-point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 polarimeter. $^1$H-N.m.r. spectra were recorded, unless otherwise stated, at 90 MHz with a Varian EM-390 spectrometer for solutions in chloroform-*d* with reference to tetramethylsilane as an internal standard, and 400 MHz spectra were recorded with a JEOL GX-400 instrument. T.l.c. was performed on plates coated with Silica Gel 60 F-254 (E. Merck, Darmstadt, G.F.R.). The silica gel used for a column chromatography was Wakogel C-300 (300 Mesh) (Wako Co., Osaka, Japan). Solvents volumes are v/v. Organic solutions were dried over anhydrous sodium sulfate and concentrated at temperatures below 50° under diminished pressure.

*1,6-Anhydro-4-*O*-(3,4-anhydro-6-deoxy-α-*D*-galactopyranosyl)-β-*D*-glucopyranose* (**3**). — To a solution of 2,3,2′,3′-tetra-*O*-acetyl-1,6-anhydro-6′-deoxy-4′-*O*-*p*-tolylsulfonyl-β-maltose[6] (**2**, 1.56 g, 2.47 mmol) in chloroform (8.7 mL) was added methanolic sodium methoxide (8.7 mL containing 50 mg of sodium), and the mixture was stirred for 4 h at 0–5°. After being made neutral with carbon dioxide, the mixture was concentrated to a syrup which was charged onto a column of silica gel that was eluted with 1:5 chloroform–methanol. The main product was recrystallized from ethanol to give 434 mg (60.5%) of **3** as prisms: m.p. 174–175°; $[\alpha]_D^{26}$ +14.5° (*c* 0.98, methanol); $^1$H-n.m.r. data: δ 5.31 (s, 1 H, H-1), 4.84 (d, 1 H, $J_{1',2'}$ 4.6 Hz, H-1′), 3.29 (s, 2 H, H-3′ and H-4′), and 1.20 (d, 3 H, *J* 6 Hz, methyl).

*Anal.* Calc. for $C_{12}H_{18}O_8$: C, 49.66; H, 6.25. Found: C, 49.87; H, 6.28.

Compound **3** was treated with acetic anhydride and pyridine overnight at room temperature. The product was purified by chromatography on silica gel with 1:5 butanone–toluene as eluant to give the triacetate (**4**) as a syrup: $[\alpha]_D^{21}$ +31.6° (*c* 1.7, chloroform); $^1$H-n.m.r. data: δ 5.40 (s, 1 H, H-1), 5.12 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1′), 4.86–4.20 (m, 5 H, H-2, H-3, H-5, H-2′, and H-5′), 4.03–3.63 (m, 2 H, $CH_2O$), 3.39 (s, 1 H, H-4), 3.27 (d, 1 H, *J* 4.8 Hz) and 3.12 (br d, *J* 4.5 Hz) (H-3′ and H-4′), 2.13 (s, 3 H), 2.09 (s, 3 H), 2.06 (s, 3 H) (OAc), and 1.32 (d, 3 H, *J* 6.3 Hz, methyl).

*Anal.* Calc. for $C_{18}H_{23}O_{11}$: C, 52.05; H, 5.58. Found: C, 51.78; H, 5.85.

*1,6-Anhydro-4-*O*-(3,4-anhydro-6-deoxy-2-*O*-tetrahydropyran-2-yl-α-*D*-galac-*

*topyranosyl)-2,3-di-O-tetrahydropyran-2-yl-β-D-glucopyranose* (**5**). — To a solution of **3** (20.3 mg, 0.0699 mmol) in dichloromethane (1 mL) was added 3,4-dihydro-2*H*-pyran (22.4 mL) and pyridinium *p*-toluenesulfonate (6.3 mg), and the mixture was stirred for 5 h at room temperature. T.l.c. (1:2 butanone–toluene) then showed conversion into a single compound ($R_F$ 0.55). The mixture was washed with saturated aqueous sodium hydrogencarbonate, dried, and evaporated. The product was purified by chromatography on silica gel to give 35.9 mg (94.6%) of **5** as a syrup: $^1$H-n.m.r. data: $\delta$ 5.50 (br s, 1 H) and 5.39 (br s, 1 H) (H-1 and H-1'), 3.11 (br s, 1 H, H-4), 2.20–1.42 (m, 27 H, tetrahydropyranyl), and 1.30 (d, 3 H, $J$ 6 Hz, methyl).

*Anal.* Calc. for $C_{27}H_{42}O_{11} \cdot 0.5\ H_2O$: C, 58.79; H, 7.86. Found: C, 58.48; H, 7.66.

*Coupling reaction of* **3** *with* DL-*4,7:5,6-di-O-isopropylidene-(1,4,6/5)-4,5,6-trihydroxy-3-hydroxymethyl-2-cyclohexenylamine* (**6**). *Preparation of* N-[*(1S)-(1,4,6/5)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenyl*]*-2,3,2',3'-tetra-O-acetyl-4'-amino-1,6-anhydro-4',6'-dideoxy-β-maltose* (**7a**) *and its diastereoisomer* (**7b**), *and* N-[*(1S)-(1,4,6/5)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenyl*]*-(1→3)-O-(2,4-di-O-acetyl-3-amino-3,6-dideoxy-α-D-gulopyranosyl)-(1→4)-2,3-di-O-acetyl-1,6-anhydro-β-D-glucopyranose* (**8a**) *and its diastereoisomer* (**8b**). — A mixture of **3** (104 mg, 0.358 mmol), **6** (86 mg, 0.36 mmol), 2-propanol (0.8 mL), and *N,N*-dimethylformamide (0.1 mL) was heated in a sealed tube for 55 h at 120°. T.l.c. then showed disappearance of **6** and formation of two components. The mixture was evaporated and the residue treated with acetic anhydride (5 mL) and pyridine (5 mL) overnight at room temperature. T.l.c. (2:7 butanone–toluene) showed two major spots ($R_F$ 0.40 and 0.37). The mixture was evaporated and the residual syrup charged on a column of silica gel that was eluted with 1:5 butanone–toluene. The first fraction gave 69 mg of a syrup that was treated with 70% aqueous acetic acid (8 mL) for 1.5 h at 55° and then evaporated. The product was acetylated conventionally and purified by chromatography to give 67.6 mg (24.0%) of **8a** as a syrup: $[\alpha]_D^{21}$ +22.7° (*c* 1.24, chloroform); $^1$H-n.m.r. data: $\delta$ 6.03 (d, 1 H, $J_{1'',2''}$ 4.5 Hz, H-2''), 3.16 (t, 1 H, $J_{2',3'} = J_{3',4'} = 4.5$ Hz, H-3'), 2.16 (s, 3 H), 2.13 (s, 3 H), 2.12 (s, 3 H), 2.07 (s, 9 H), and 2.04 (s, 6 H) (OAc), and 1.15 (d, 3 H, $J$ 6.3 Hz, methyl).

*Anal.* Calc. for $C_{34}H_{47}NO_{20}$: C, 51.71; H, 6.00; N, 1.77. Found: C, 51.98; H, 5.89; N; 1.71.

The second fraction gave 144 mg of a syrup that was treated with 70% aqueous acetic acid (14 mL) for 1.5 h at 55°. The product was acetylated and fractionated by chromatography on silica gel with 1:2 acetone–hexane as eluant. The first fraction gave crystals that were recrystallized from ethanol to give 89.8 mg (31.8%) of **8b** as needles: m.p. 182–183° $[\alpha]_D^{25}$ −7.5° (*c* 0.96, chloroform); $^1$H-n.m.r. data: $\delta$ 6.23 (d, 1 H, $J_{1'',2''}$ 6 Hz, H-2''), 3.46 (br s, 1 H, H-4), 3.03 (t, 1 H, $J_{2',3'} = J_{3',4'} = 4.5$ Hz, H-3'), 2.17 (s, 3 H), 2.14 (s, 9 H), 2.11 (s, 3 H), 2.09 (s, 3 H), and 2.02 (s, 6 H) (OAc), and 1.14 (d, 3 H, $J$ 6.3 Hz, methyl).

*Anal.* Calc. for $C_{34}H_{47}NO_{20}$: C, 51.71; H, 6.00; N, 1.77. Found: C, 51.92; H, 5.86; N, 1.84.

The second fraction gave 17.2 mg (6.1%) of **7a** as a syrup: $[\alpha]_D^{19}$ +52.2° (*c* 0.73, chloroform); $^1$H-n.m.r. data: $\delta$ 6.00 (d, 1 H, $J_{1'',2''}$ 6 Hz, H-2''), 3.41 (br s, 1 H, H-4), 2.43 (t, 1 H, $J_{3',4'} = J_{4',5'} = 10$ Hz, H-4'), 2.16 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.05 (s, 6 H), and 2.03 (s, 9 H) (OAc), and 1.21 (d, 3 H, *J* 6 Hz, methyl).

*Anal.* Calc. for $C_{34}H_{47}NO_{20}$: C, 51.71; H, 6.00; N, 1.77. Found: C, 51.52; H, 5.88; N, 1.56.

The third fraction gave 16 mg (5.7%) of **7b** as a syrup: $[\alpha]_D^{23}$ −1.6° (*c* 0.82, chloroform); $^1$H-n.m.r. data: $\delta$ 5.86 (d, 1 H, $J_{1'',2''}$ 5.8 Hz, H-2''), 3.40 (br s, 1 H, H-4), 2.48 (t, 1 H, $J_{3',4'} = J_{4',5'} = 10$ Hz, H-4'), 2.18 (s, 3 H), 2.10 (s, 9 H), 2.06 (s, 6 H), 2.04 (s, 3 H), and 2.02 (s, 3 H) (OAc), and 1.40 (d, 3 H, *J* 6.3 Hz, methyl).

*Anal.* Calc. for $C_{34}H_{47}NO_{20}$: C, 51.71; H, 6.00; N, 1.77. Found: C, 52.02; H, 6.04; N, 1.58.

*Coupling reaction of* **5** *with* **6**. — A mixture of **5** (139 mg, 0.260 mmol), **6** (66.7 mg, 0.276 mmol), and 2-propanol (0.5 mL) was heated in a sealed tube for 80 h at 120°. The brown mixture was evaporated and the residue was treated with 70% aqueous acetic acid (20 mL) for 1.5 h at 55°. The products were then acetylated and fractionated by a silica gel column, eluting with 1:2 acetone–hexane. The first fraction gave 10.7 mg (5.3%) of **7a** as a syrup: $[\alpha]_D^{15}$ +52.3° (*c* 0.48, chloroform). The second fraction gave 9.3 mg (4.6%) of **7b** as a syrup: $[\alpha]_D^{14}$ −2.2° (*c* 1.06, chloroform). The third fraction gave 110 mg of a crystalline mixture of **8a** and **8b**. Fractional recrystallization from ethanol gave 48.6 mg (24.2%) of **8b** as needles: $[\alpha]_D^{15}$ −8.6° (*c* 0.98, chloroform). All compounds were shown to be identical with those obtained by the reaction of **3** with **6**.

N-[*(1S)-(1,4,6/5)-4,5,6-triacetoxy-3-acetoxymethyl-2-cyclohexenyl*]-*1,2,3,6,-2',3'-hexa*-O-*acetyl-4'-amino-4',6'-dideoxy-α- maltose* (**9a**). — Compound **7a** (14.9 mg, 0.0189 mmol) was treated with a mixture of reagents [acetic acid–acetic anhydride–conc. sulfuric acid (30:70:1)] (0.6 mL) for 3 h at room temperature. The mixture was then poured into ice–water and extracted with ethyl acetate (25 mL). The extracts were washed with saturated aqueous sodium hydrogencarbonate and water, and dried. Removal of the solvent gave 14.7 mg (87.5%) of **9a** slightly contaminated with the $\beta$ anomer as a syrup: $[\alpha]_D^{21}$ +95.4° (*c* 0.49, chloroform); $^1$H-n.m.r. data (400 MHz): $\delta$ 6.24 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1$\alpha$), 5.96 (d, 1 H, $J_{1'',2''}$ 4.6 Hz, H-2''), 5.73 (d, trace, $J_{1,2}$ 8.3 Hz, H-1$\beta$), 5.60 (d, 1 H, $J_{4'',5''}$ 6.7 Hz, H-4''), 5.56 (dd, 1 H, $J_{5'',6''}$ 10.1 Hz, H-5''), 5.49 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 8.6 Hz, H-3), 5.26 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1'), 5.13 (t, 1 H, $J_{2',3'} = J_{3',4'} = 10.1$ Hz, H-3'), 4.97 (dd, 1 H, H-2), 4.93 (dd, 1 H, $J_{1'',6''}$ 4.6 Hz, H-6''), 4.80 (dd, 1 H, H-2'), 4.66 (d, 1 H, $J_{gem}$ 13.1 Hz) and 4.38 (d, 1 H) (C*H*$_2$OAc, cyclohexene part), 4.47 (dd, 1 H, $J_{gem}$ 12.1, $J_{5,6}$ 3 Hz) and 4.21 (dd, 1 H, $J_{5,6'}$ 3.4 Hz) (C*H*$_2$OAc, sugar part), 4.20 (br d, 1 H, $J_{4,5}$ 8.6 Hz, H-5), 4.04 (t, 1 H, H-4), 3.72 (t, 1 H, H-1''), 3.53 (dd, 1 H, $J_{4',5'}$ 10.1, $J_{5',6'}$ 6.1 Hz, H-5'), 2.40 (t, 1 H, H-4'), 2.22 (s, 3 H), 2.14 (s, 3 H), 2.11 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 2.00 (s, 3 H), and 1.99 (s, 3 H) (OAc), and 1.21 (d, 3 H, *J* 6.1 Hz, methyl).

*Anal.* Calc. for $C_{38}H_{53}NO_{23}$: C, 51.18; H, 5.99; N, 1.57. Found: C, 51.41; H, 5.97; N, 1.59.

The $^1$H-n.m.r. spectrum (400 MHz in chloroform-*d*) was shown to be superposable on that of an authentic sample[2,4].

N-[*(1R)-(1,4,6/5)-4,5,6-Triacetoxy-3-acetoxymethyl-2-cyclohexenyl*]-*1,2,3,6,-2',3'-hexa*-O-*acetyl-4'-amino-4',6'-dideoxy-α-maltose* (**9b**). — Compound **7b** (10.2 mg, 0.0129 mmol) was subjected to acetolysis as in the preparation of **9a** to give 8.9 mg (77%) of **9b** slightly contaminated with the β anomer as a syrup: $[\alpha]_D^{21}$ +47.4° (*c* 0.32, chloroform); $^1$H-n.m.r. data (400 MHz): δ 6.24 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1α), 5.81 (d, 1 H, $J_{1'',2''}$ 5.5 Hz, H-2''), 5.73 (d, trace, $J_{1,2}$ 8.3 Hz, H-1β), 5.56 (d, 1 H, $J_{4'',5''}$ 6.7 Hz, H-4''), 5.53 (dd, 1 H, $J_{5'',6''}$ 10.4 Hz, H-5''), 5.49 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 9.6 Hz, H-3), 5.29 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1'), 5.12 (t, 1 H, $J_{2',3'} = J_{3',4'} = 10.1$ Hz, H-3'), 4.97 (dd, 1 H, H-2), 4.96 (dd, 1 H, $J_{1',6'}$ 5.5 Hz, H-6''), 4.75 (dd, 1 H, H-2'), 4.64 (d, 1 H, $J_{gem}$ 13.1 Hz) and 4.35 (d, 1 H) ($CH_2$OAc, cyclohexene part), 4.47 (br d, 1 H, $J_{gem}$ 12.2, $J_{5,6}$ 3.2 Hz, H-6), 4.08 (br d, 1 H, $J_{4,5}$ 6.4 Hz, H-5), 4.05 (dd, 1 H, H-4), 3.73 (t, 1 H, $J_{1'',2''}$ 5.5 Hz, H-1''), 3.53 (m, 1 H, H-5'), 2.45 (t, 1 H, $J_{4',5'}$ 10.1 Hz, H-4'), 2.22 (s, 3 H), 2.14 (s, 3 H), 2.10 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 2.01 (s, 3 H), and 1.99 (s, 3 H) (OAc), and 1.36 (d, 3 H, *J* 6.1 Hz, methyl).

*Anal.* Calc. for $C_{38}H_{53}NO_{23}$: C, 51.18; H, 5.99; N, 1.57. Found: C, 51.19; H, 5.92; N, 1.49.

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