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Chemical Modification of Lactose. XI.[1] A New Synthesis of 2-Acetamido-2-deoxy-4-O-β-D-galactopyranosyl-α-D-glucopyranose (*N*-Acetyllactosamine)

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A new synthetic route of *N*-acetyllactosamine is described. This starts from 2-O-tosylate or 2,3′-di-O-tosylate of 1,6-anhydro-4′,6′-O-benzylidene-β-lactose (**1**), which is the primary or the secondary major product of partial tosylation of compound **1** as reported in Part VIII of this series (T. Takamura and S. Tejima, *Chem. Pharm. Bull.* (Tokyo), **26**, 1117 (1978)). The final product is isolated in about 10% yield from compound **1** *via* the following series of reaction: 1), monoepoxide formation, 2), azidolysis of the epoxide, 3), acetolysis of the azido sugar, 4), reduction of the azido group to amino group, followed by acetylation, and 5), de-O-acetylation.

Keywords——new synthesis; N-acetyllactosamine; lactosan; monoepoxide; azidolysis; trans-diaxial cleavage; detosylation; acetolysis

N-Acetyllactosamine is not only the major repeating unit in keratosulfates,[3] but also a component of the sugar moiety in α_1-acid glycoprotein or blood-group substances.[4] Higher oligosaccharides in human milk, such as lacto-*N*-neotetraose[5] or para-lacto-*N*-hexaose,[6] also comprise *N*-acetyllactosamine as the constituent.

As to chemical synthesis of *N*-acetyllactosamine, three main routes have been known: 1), Hydrogenation of lactose phenylosazone with hydrogen in the presence of a palladium-carbon catalyst, and subsequent acetylation and de-O-acetylation of the hydrogenation product afford a little of *N*-acetyllactosamine with a large amount of 1-acetamido-1-deoxy-lactulose.[7] 2), Addition of hydrogen cyanide to 3-O-β-D-galactopyranosyl-D-arabinosyl phenylamine furnishes α-phenylaminonitrile. Subsequent catalytic partial hydrogenation of the nitrile in the presence of dilute hydrochloric acid gives rise to lactosamine hydrochloride, which is turned into *N*-acetyllactosamine.[8] 3), Condensation of partially protected benzyl *N*-acetyl-α-D-glucosaminide derivatives with acetylated orthoester of D-galactose[9] or acetobromogalactose,[10] and removal of the protecting groups of the condensates.

In Part VIII of this series,[11] we reported synthesis of several partial *p*-toluenesulfonylation (tosylation) products of 1,6-anhydro-4′,6′-O-benzylidene-β-lactose (**1**). In this paper a new synthetic route of *N*-acetyllactosamine from lactose is described. Our route starts from the major product of the partial tosylation of **1** and proceeds *via* the following series of reactions: 1), epoxide formation, 2), azidolysis of the epoxide, 3), acetolysis of the azido sugar,

1) Part X: T. Chiba and S. Tejima, *Chem. Pharm. Bull.* (Tokyo), **26**, 3426 (1978).
2) Location: *Tanabe-dori, Mizuho-ku, Nagoya, 467, Japan.*
3) V.P. Bhavanandan and K. Meyer, *J. Biol. Chem.*, **242**, 4352 (1967).
4) A. Gottschalk (ed.) "Glycoproteins," Elsevier Publishing Company, Amsterdam, London, and New York, 1972.
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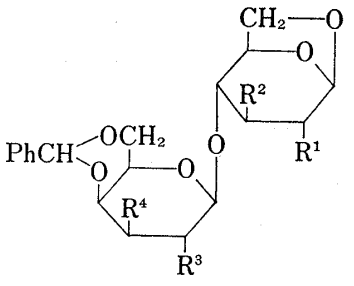
9) *a*) S.E. Zurabyan, E.N. Lopantseva, and A.Ya. Khorlin, *Dokl. Akad. Nauk SSSR*, **210**, 1216 (1973) [*C.A.*, **79**, 105492*w* (1973)]; *b*) J.-C. Jacquinet and P. Sinaÿ, *Carbohyd. Res.*, **46**, 138 (1976).
10) A.Ya. Khorlin, V.A. Nesmeyanov, and S.E. Zurabyan, *Carbohyd. Res.*, **33**, C1—C3 (1974).
11) T. Takamura and S. Tejima, *Chem. Pharm. Bull.* (Tokyo), **26**, 1117 (1978).

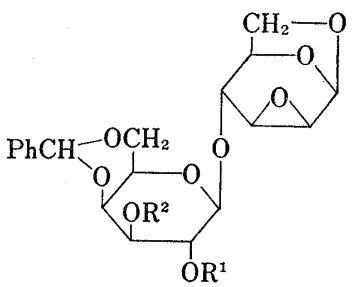
4), reduction of the azido group to amino group, following acetylation, and 5), de-O-acetylation. We report the results in full detail.

Crystalline 1,6-anhydro-4′,6′-O-benzylidene-2-O-tosyl-β-lactose (**2**) is the primary major product of partial tosylation of **1**. It was isolated in 25.2% yield by the selective tosylation of **1** using 2.2 molar equivalents of tosyl chloride in pyridine at 0°.[11] The tosyloxy group and hydroxyl group in the D-glucose moiety in compound **2** are *trans*-diaxial. Thus, the epoxide ring formation proceeded very smoothly by reacting compound **2** with a theoretical amount of sodium methoxide in methanol at room temperature overnight. The epoxide was isolated as a crystalline diacetate, 1,6:2,3-dianhydro-4-O-(2,3-di-O-acetyl-4,6-O-benzylidene-β-D-galactopyranosyl)-β-D-mannopyranose (**5**), in 90.4% yield. Treatment of **5** with sodium methoxide in methanol yielded deacetylated epoxide, 1,6:2,3-dianhydro-4-O-(4,6-O-benzylidene-β-D-galactopyranosyl)-β-D-mannopyranose (**6**), as white needles in 91.9% yield.

Compound **5**, a key intermediate of our route, was also available from 1,6-anhydro-4′,6′-O-benzylidene-2,3′-di-O-tosyl-β-lactose (**3**) *via* monoepoxide formation, detosylation, and acetylation. Compound **3** is obtainable in 21.9% yield as the secondary major product of the partial tosylation of **1**.[11] In compound **3**, the tosyloxy group and the hydroxyl group in the D-glucose moiety are *trans*-diaxial and those in the D-galactose are *trans*-diequatorial. Thus, when **3** was treated with a theoretical amount of sodium methoxide in methanol and pyridine at room temperature, selective epoxide formation occurred in the D-glucose moiety to afford monoepoxide having a tosyloxy group in the D-galactose moiety. The monoepoxide, 1,6:2,3-dianhydro-4-O-(4,6-O-benzylidene-3-O-tosyl-β-D-galactopyranosyl)-β-D-mannopyranose (**4**), was isolated as white needles in 95.3% yield. Treatment of **4** with 2% sodium amalgam at 0° proceeded detosylation smoothly. But the detosylation of **4** at room temperature resulted in the formation of unidentified by-products. The detosylated monoepoxide was isolated as a diacetate (**5**) in 84.8% yield from **4**, which was indistinguishable in their mixed melting point, specific rotation, nuclear magnetic resonance (NMR) and infrared (IR) spectra from the product prepared from **2**.

Azidolysis of the epoxide ring in **5** was performed by heating a mixture of **5** and sodium azide in aqueous hexamethylphosphoric triamide (HMPA) in the presence of ammonium chloride at 110° for 42 hours. The resulting azidolysis product was isolated as a crystalline triacetate, 2′,3,3′-tri-O-acetyl-1,6-anhydro-2-azido-4′,6′-O-benzylidene-2-deoxy-β-lactose (**7**),in 52.2% yield from **5**. Epoxides attached to the rigid 1,6-anhydro system are known to undergo scission by a nitrogen nucleophile to lead predominantly to *trans*-diaxial substitution.[12] In azidolysis of **5**, *trans*-diaxial cleavage occurred stereospecifically to afford **7** as the sole reaction product. No other product could be observed by thin-layer chromatography (TLC).





1: $R^1=R^2=R^3=R^4=OH$
2: $R^1=OTs$, $R^2=R^3=R^4=OH$
3: $R^1=R^4=OTs$, $R^2=R^3=OH$
7: $R^1=N_3$, $R^2=R^3=R^4=OAc$

4: $R^1=H$, $R^2=Ts$
5: $R^1=R^2=Ac$
6: $R^1=R^2=H$

Ac=acetyl, Ph=phenyl, Ts=tosyl

Chart 1

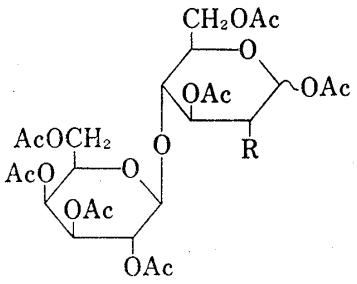
Acetolysis of **7** cleaved the 1,6-anhydro ring and benzylidene group simultaneously to afford an anomeric mixture of fully acetylated azido sugar, 1,2′,3,3′,4′,6,6′-hepta-O-acetyl-2-azido-2-deoxy-lactose. The anomeric mixture (**8**), $[\alpha]_D^{20}$ +57.1°, was fractionated through a column of silica gel. From the faster moving effluent, the β-anomer, 1,2′,3,3′,4′,6,6′-hepta-O-acetyl-2-azido-2-deoxy-β-lactose (**9**) was recovered and crystallized from ethanol as colorless prisms having $[\alpha]_D^{23}$ +2.5°. In the NMR spectrum, the anomeric proton in the D-glucose moiety appeared at 5.27 ppm as a doublet with $J_{1,2}$=8.5 Hz.

The α-anomer, 1,2′,3,3′,4′,6,6′-hepta-O-acetyl-2-azido-2-deoxy-α-lactose (**10**), was eluted from the column after elution of the β-anomer. After evaporation of the solvent and crystallization of the residue from ethanol, compound **10** was isolated as colorless needles having $[\alpha]_D^{22}$ +77.9°. In the NMR spectrum, the anomeric proton in the D-glucose moiety appeared at 6.17 ppm as a doublet with $J_{1,2}$=3.5 Hz. Thus, as each anomer was separated in a pure state, the ratio α: β in **8** was estimated to be almost 7: 3 by the degree of the specific rotations of **8**, **9**, and **10**.

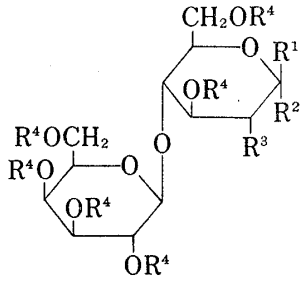
Reduction of acetylated azido sugar to acetylated amino sugar was performed smoothly. Namely, compound **8** in methanol was hydrogenated in the presence of Raney nickel catalyst at room temperature under atmospheric pressure. After acetylation, the amino sugar was separated as the anomeric mixture of acetate (**11**) in 92.8% yield. The α-anomer, 2-acetamido-1,3,6-tri-O-acetyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranose (**12**), was isolated by passing **11** through a column of silica gel. Evaporation of the solvent and treatment of the residue with 2-propanol gave **12** as short needles in 46.5% yield. In the NMR spectrum of **12**, the anomeric proton in the D-glucose moiety appeared at 6.09 ppm as a doublet with $J_{1,2}$=3.5 Hz. Melting point and specific rotation of **12** were in good agreement with the reported values.[9b,12b] But the β-anomer could not be isolated.

The product **11** was deacetylated with sodium methoxide in methanol. The resulting deacetylated product was crystallized from a mixture of 2-propanol and methanol to give 2-acetamido-2-deoxy-4-O-β-D-galactopyranosyl-α-D-glucopyranose (**13**) in 73.6%. Compound **13** showed mp 173° and $[\alpha]_D^{19}$ +48.3° (3 min)→+29.7° (3 hr), which were in good agreement with the reported values.[7,8,9b] In addition, an authentic sample of *N*-acetyllactosamine and **13** showed the same mobility on paper partition chromatography (PPC) and TLC.

In conclusion, crystalline *N*-acetyllactosamine could be synthesized in about 10% yield from **1** without the use of tedious procedures. All intermediates are crystallized throughout the route.



8: R=N_3
11: R=NHAc



9: R^1=OAc, R^2=H, R^3=N_3, R^4=Ac
10: R^1=H, R^2=OAc, R^3=N_3, R^4=Ac
12: R^1=H, R^2=OAc, R^3=NHAc, R^4=Ac
13: R^1=R^4=H, R^2=OH, R^3=NHAc

Chart 2

12) *a*) A. Fuerst and P.A. Plattner, *Proc. Int. Congr. Pure Appl. Chem.*, **1951** 409; *b*) Y. Rabinsohn, A.J. Acher, and D. Shapiro, *J. Org. Chem.*, **38**, 202 (1973).

Experimental

Instruments used in the experimental section and the conditions for chromatography were same as reported before,[11] unless otherwise indicated. TLC was performed with solvent combination (v/v): (A), $CHCl_3$–acetone (3:1); (B), $CHCl_3$–acetone (1:1); (C), benzene–ether (1:2); (D), CH_2Cl_2–acetone (9:1). PPC was performed by the ascending method[13] with BuOH–pyridine–H_2O (6:4:3, v/v), and detection was effected with (A), aniline hydrogen phthalate,[14] (B), alkaline silver nitrate,[15] and (C), 0.2% ninhydrin dissolved in BuOH saturated with H_2O.[16]

1,6:2,3-Dianhydro-4-O-(4,6-O-benzylidene-3-O-tosyl-β-D-galactopyranosyl)-β-D-mannopyranose (4)——To a solution of 3[11] (15 g, 20.8 mmol) in a mixture of dry MeOH (150 ml) and dry pyridine (90 ml), 0.5 N methanolic NaOMe (45.6 ml, 22.8 mmol) was added dropwise with stirring at room temperature, and the stirring was continued overnight. The mixture was neutralized with glacial AcOH, evaporated to dryness, and the residue was stirred with CH_2Cl_2 (150 ml) and H_2O (150 ml) to make dissolution. The organic layer was separated, washed with H_2O (150 ml × 3), dried over $MgSO_4$, and filtered. Removal of the solvent from the filtrate gave a sirupy residue which was crystallized from MeOH. Recrystallization from MeOH afforded white needles (10.88 g, 95.3%), mp 185—187°, $[\alpha]_D^{24}$ +8.2° (c=0.9, pyridine). IR ν_{max}^{Nujol} cm^{-1}: 3550 (OH). NMR $\delta_{ppm}^{C_5D_5N}$: 2.17 (3H, s, $C_6H_4CH_3$), 5.81 (1H, d, $J_{1,2}$=3 Hz, H-1, β-Man). TLC: *Rf* 0.29 (solvent A), 0.51 (B), 0.07 (C), 0.22 (D). *Anal.* Calcd. for $C_{26}H_{28}O_{11}S$: C, 56.93; H, 5.14. Found: C, 56.77; H, 5.18.

1,6:2,3-Dianhydro-4-O-(2,3-di-O-acetyl-4,6-O-benzylidene-β-D-galactopyranosyl)-β-D-mannopyranose (5)——1) From Compound 2: To a suspension of 2[11] (2.2 g, 3.88 mmol) in dry MeOH (50 ml), 0.5 N methanolic NaOMe (8.50 ml, 4.26 mmol) was added dropwise with stirring at room temperature, during which white precipitate appeared after a homogeneous solution had been obtained. The stirring was continued overnight. Then the mixture was neutralized with glacial AcOH and evaporated to dryness. The residue was acetylated with Ac_2O (15 ml) and pyridine (15 ml) overnight at 5°. The mixture was concentrated to a sirup by repeated co-distillation with toluene. A solution of the residue in CH_2Cl_2 was washed with H_2O, 10% H_2SO_4, H_2O, satd. $NaHCO_3$, and H_2O, successively, then dried over $CaCl_2$, and concentrated to dryness. The residue was crystallized from EtOH. Recrystallization from EtOH gave white needles (1.68 g, 90.4%), mp 208—210°, $[\alpha]_D^{22}$ +26.6° (c=0.98, $CHCl_3$). The Ross test[17] of the product was positive. NMR $\delta_{ppm}^{CDCl_3}$: 2.08 (6H, s, OAc × 2). TLC: *Rf* 0.39 (solvent A), 0.52 (B), 0.09 (C), 0.37 (D). *Anal.* Calcd. for $C_{23}H_{26}O_{11}$: C, 57.74; H, 5.48. Found: C, 57.74; H, 5.58.

2) From Compound 4: To a suspension of compound 4[11] (1 g) in dry MeOH (50 ml), 2% Na–Hg (14 g) was added with stirring at 0°, and the stirring was continued for 1 hr. Then the temperature was raised to 8°, and the stirring was continued for a further 40 hr. The mixture was neutralized with glacial AcOH, concentrated to dryness, and the residue was acetylated with Ac_2O (20 ml) and pyridine (20 ml). The mixture was processed as described in 1) to afford diacetate (740 mg, 84.8%), which was indistinguishable (mixed mp, IR spectrum, and TLC) from the product prepared from compound 2.

1,6:2,3-Dianhydro-4-O-(4,6-O-benzylidene-β-D-galactopyranosyl)-β-D-mannopyranose (6)——To a suspension of 5 (80 mg) in dry MeOH (2 ml), 0.5 N methanolic NaOMe (0.05 ml) was added dropwise with stirring at room temperature, and the stirring was continued with the exclusion of moisture for 2 hr. Deacetylation was monitored by TLC (solvent A). The reaction mixture was neutralized with dry Amberlite IR-120 (H^+) resin and then filtered. Removal of the solvent and recrystallization of the residue from MeOH gave white needles (60.6 mg, 91.9%), mp 215—217°, $[\alpha]_D^{23}$ −42.2° (c=0.86, acetone). The Ross test[17] of the product was positive. IR ν_{max}^{Nujol} cm^{-1}: 3420 (OH). TLC: *Rf* 0.03 (solvent A), 0.11 (B). *Anal.* Calcd. for $C_{19}H_{22}O_9 \cdot 1/2H_2O$: C, 56.57; H, 5.75. Found: C, 56.64; H, 5.91.

2′,3,3′-Tri-O-acetyl-1,6-anhydro-2-azido-4′,6′-O-benzylidene-2-deoxy-β-lactose (7)——A mixture of 5 (1.5 g, 3.14 mmol), NaN_3 (1.5 g, 23.1 mmol), and NH_4Cl (515 mg, 9.36 mmol) in a mixture of HMPA (60 ml) and H_2O (6 ml) was heated in an oil bath at 110° for 42 hr. After cooling to room temperature, H_2O (200 ml) was added, and the solution was extracted with AcOEt (100 ml × 3), dried (Na_2SO_4), and evaporated to dryness. The residue was acetylated with Ac_2O (10 ml) and pyridine (10 ml) as described for compound 5. The acetate was recrystallized from MeOH to give colorless needles (922 mg, 52.2%), mp 219—220°, $[\alpha]_D^{26}$ +49.6° (c=0.82, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 2160, 2120 (N_3). NMR $\delta_{ppm}^{CDCl_3}$: 2.08 (6H, s, OAc × 2), 2.10 (3H, s, OAc). TLC: *Rf* 0.38 (solvent A), 0.54 (B), 0.09 (C), 0.32 (D). *Anal.* Calcd. for $C_{25}H_{29}N_3O_{12}$: C, 53.29; H, 5.19; N, 7.46. Found: C, 53.54; H, 5.05; N, 7.23.

Anomeric Mixture of 1,2′,3,3′,4′,6,6′-Hepta-O-acetyl-2-azido-2-deoxy-lactose (8)——To compound 7 (600 mg), a chilled acetolysis mixture (11 ml, H_2SO_4–Ac_2O–AcOH, 1:70:30, v/v) was added dropwise with

13) M. Ueda, *Yakugaku Zasshi*, **90**, 1322 (1970).
14) S.M. Partridge, *Nature* (London), **164**, 443 (1949).
15) W.E. Trevelyan, D.P. Procter, and J.S. Harrison, *Nature* (London), **166**, 444 (1950).
16) D. Aminoff and W.T.J. Morgan, *Nature* (London), **162**, 579 (1948); A.R. Patton and P. Chism, *Anal. Chem.*, **23**, 1683 (1951).
17) W.C.J. Ross, *J. Chem. Soc.*, **1950**, 2257.

stirring at 0°, and the stirring was continued for 2 hr at room temperature. The solution was poured into ice-H_2O with stirring, and the stirring was continued overnight. The mixture was extracted with CH_2Cl_2 (30 ml×3). The organic layer was washed with aq. $NaHCO_3$ and H_2O, successively, then dried over $CaCl_2$, and evaporated to dryness. A solution of the residue in CH_2Cl_2 (10 ml) was purified through a column of silica gel by elution with $CHCl_3$–acetone (35: 1, v/v). Removal of the solvent gave **8** as a white powder (467 mg, 66.3%), mp 72—75°, $[\alpha]_D^{20}$ +57.1°. The ratio α: β in **8** was 7: 3 by the degree of the specific rotations of **8**, **9**, and **10**.

1,2′,3,3′,4′,6,6′-Hepta-O-acetyl-2-azido-2-deoxy-β-lactose (**9**)——A solution of **8** (400 mg) in CH_2Cl_2 (5 ml) was chromatographed through a column of silica gel by elution with benzene-ether (1: 1, v/v) to afford the faster-moving product, **9** (100 mg, 25%) as a sirup. It was crystallized from EtOH to yield colorless prisms, mp 75—78°, $[\alpha]_D^{23}$ +2.5° (c=0.52, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 2120 (N_3). NMR $\delta_{ppm}^{CDCl_3}$: 1.94, 2.01, 2.06, 2.10, 2.12, 2.15, 2.17 (21H, each s, OAc×7), 5.27 (1H, d, $J_{1,2}$=8.5 Hz, H-1, β-Glc). TLC: *Rf* 0.26 (solvent C). *Anal.* Calcd. for $C_{26}H_{35}N_3O_{17}$: C, 47.21; H, 5.33; N, 6.35. Found: C, 46.93; H, 5.30; N, 6.30.

1,2′,3,3′,4′,6,6′-Hepta-O-acetyl-2-azido-2-deoxy-α-lactose (**10**)——In the column chromatography of **8**, compound **10** was eluted with the same solvent after **9** had emerged. After removal of the solvent and treatment of the residue with EtOH, **10** was crystallized as colorless needles (250 mg, 63%), mp 73—75°, $[\alpha]_D^{22}$ +77.9° (c=0.94, $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 2115 (N_3). NMR $\delta_{ppm}^{CDCl_3}$: 1.95, 2.03, 2.05, 2.09, 2.11, 2.15, 2.18 (21H, each s, OAc×7), 6.17 (1H, d, $J_{1,2}$=3.5 Hz, H-1, α-Glc). TLC: *Rf* 0.22 (solvent C). *Anal.* Calcd. for $C_{26}H_{35}N_3O_{17}$: C, 47.21; H, 5.33; N, 6.35. Found: C, 47.01; H, 5.20; N, 6.34.

Anomeric Mixture of 2-Acetamido-1,3,6-tri-O-acetyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-glucopyranose (**11**)——A solution of **8** (1 g) in MeOH (70 ml) was hydrogenated in the presence of freshly prepared Raney Ni catalyst overnight at room temperature under atmospheric pressure. After removal of the catalyst by filtration and washing of the residue with MeOH, the combined filtrate was evaporated to dryness to afford an amorphous powder (830 mg), which was acetylated with Ac_2O (10 ml) and pyridine (10 ml). The mixture was processed as described for compound **5** to yield **11** as an amorphous powder (950 mg, 92.8%).

2-Acetamido-1,3,6-tri-O-acetyl-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranose (**12**)——A solution of **11** (950 mg) in CH_2Cl_2 (10 ml) was chromatographed through a column of silica gel by elution with $CHCl_3$–acetone (10: 1, v/v). Compound **12** was isolated as an amorphous powder, which was crystallized from 2-PrOH as short needles (442 mg, 46.5%), mp 230—231°, $[\alpha]_D^{22}$ +50.1° (c=0.96, $CHCl_3$). NMR $\delta_{ppm}^{CDCl_3}$: 1.91, 1.95, 2.06, 2.08, 2.10, 2.15, 2.17 (24H, each s, OAc×7, NAc), 5.78 (1H, d, $J_{NH,2}$= 9 Hz, NH), 6.09 (1H, d, $J_{1,2}$=3.5 Hz, H-1, α-Glc). (lit.[9b] mp 224—225°, $[\alpha]_D^{20}$ +58° (c=1, $CHCl_3$); lit.[12b] mp 223—225°, $[\alpha]_D^{25}$ +57.9°).

2-Acetamido-2-deoxy-4-O-β-D-galactopyranosyl-α-D-glucopyranose (**N-Acetyllactosamine**) (**13**)——To a solution of **11** (370 mg) in dry MeOH (10 ml), 0.5 N methanolic NaOMe (0.5 ml) was added with stirring at room temperature. The mixture was proceeded as described for compound **6** to afford *N*-acetyllactosamine (**13**), which was crystallized from 2-PrOH–MeOH (154 mg, 73.6%). The product had mp 173° and $[\alpha]_D^{19}$ +48.3° (3 min)→+29.7° (3 hr) (c=0.71, H_2O) (lit.[7] mp 168—170°, $[\alpha]_D^{23}$ +50.5°→+28.5° (c=0.98, H_2O); lit.[9b] mp 170—171°, $[\alpha]_D^{20}$ +50°→+28.5° (c=0.6, H_2O–MeOH (9: 1, v/v); lit.[18] mp 172°, $[\alpha]_D^{25}$ +51.2° (0 min)→ +27.8° (3 hr) (c=1, H_2O). TLC: *Rf* 0.27 (70% 2-PrOH–AcOEt (2: 1, v/v)); *Rf* 0.28 (BuOH–EtOH–H_2O (5: 3: 2, v/v)), indistinguishable from an authentic *N*-acetyllactosamine. PPC: *Rf* 0.20 (BuOH–benzene–pyridine–H_2O (5: 1: 3: 3, v/v, upper layer)), indistinguishable from authentic *N*-acetyllactosamine.

PPC of Acid Hydrolyzate of Compound 13——A mixture of **13** (20 mg) and 1 N HCl (4 ml) in a sealed tube was heated at 95° for 2 hr, and evaporated to dryness. A trace of HCl was completely removed by repeated co-distillation with EtOH. The residue was dissolved in a small amount of H_2O, and subjected to PPC in which galactose (R_{Glc} 0.88) and glucosamine hydrochloride (R_{Glc} 0.79) were identified.

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