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SYNTHESIS OF A 2-ACETAMIDO-5-AMINO-2,5-DIDEOXY-D-XYLOPYRANOSYL DERIVATIVE*

AKIRA HASEGAWA, NOBUMITSU ARITAKE, AND MAKOTO KISO
Department of Agricultural Chemistry, Gifu University, Kakamigahara, Gifu 504 (Japan)
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ABSTRACT

2-Acetamido-5-amino-2,5-dideoxy-D-xylopyranosyl hydrogensulfite (**11**) has been synthesized from benzyl 2-(benzyloxycarbonylamino)-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside (**1**). *O*-Deisopropylidenation of **1** gave the triol **2**, which was converted, *via* oxidative cleavage at C-5–C-6 and subsequent reduction, into the related benzyl β-D-xylofuranoside derivative (**3**). Catalytic reduction of benzyl 2-(benzyloxycarbonylamino)-2-deoxy-5-*O*-tosyl-β-D-xylofuranoside, derived from **3** by selective tosylation, and subsequent *N*-acetylation, afforded benzyl 2-acetamido-2-deoxy-5-*O*-tosyl-β-D-xylofuranoside, which was treated with sodium azide to give the corresponding 5-azido derivative (**6**). (Tetrahydropyran-2-yl)ation of the product formed by hydrolysis of **6** gave 2-acetamido-5-azido-2,5-dideoxy-1,3-di-*O*-(tetrahydropyran-2-yl)-D-xylofuranose (**9**). Treatment of 2-acetamido-5-amino-2,5-dideoxy-1,3-di-*O*-(tetrahydropyran-2-yl)-D-xylofuranose, derived from **9** by reduction, with sulfur dioxide in water gave **11**. Hydrogenation of **6** and subsequent acetylation yielded 3-acetamido-4,5-diacetoxy-1-acetyl-*xylo*-piperidine. Evidence in support of the structures assigned to the new derivatives is presented.

INTRODUCTION

There has been a great deal of activity in recent years in the synthesis of hetero-sugars, in which the ring-oxygen atom of aldoses has been replaced by nitrogen, phosphorus, or sulfur. These sugars are interesting, not only from the point of view of the chemistry involved, but also for their various, biological activities. The synthesis and chemistry of 4(or 5)-aminoaldoses have been well studied[2,3], but, as far as we are aware, no report has appeared on the synthesis of 2-amino sugar derivatives having nitrogen in the ring.

In previous papers[4,5], we have shown that various *N*-substituted 2-amino-2-deoxy-D-aldohexoses react with 2,2-dialkoxypropane–*N*,*N*-dimethylformamide–*p*-toluenesulfonic acid at 80–90°, to give the corresponding 5,6-*O*-isopropylidene-D-

*Studies on Hetero Sugars, Part IV. For Part III, see ref. 1.

aldofuranosides. The potential utility of this reagent for syntheses in the field of amino sugars was emphasized, and such biologically important amino sugar derivatives as Prumycin and 2-acetamido-2-deoxy-5-thio-D-glucose have been synthesized[1,6-9]. The present report describes a synthesis of 2-acetamido-5-amino-2,5-dideoxy-D-xylopyranosyl hydrogensulfite.

RESULTS AND DISCUSSION

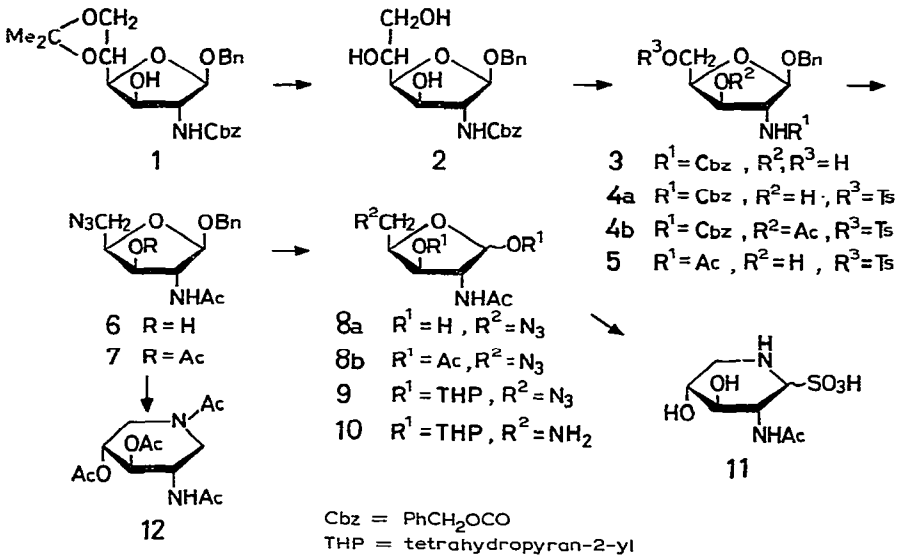
Benzyl 2-(benzyloxycarbonylamino)-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside[5] (**1**) was converted into the triol **2** on partial hydrolysis with 60% aqueous acetic acid at 40°. Oxidative cleavage between C-5 and C-6 of compound **2** with sodium metaperiodate gave a syrupy aldehyde, which was reduced with sodium borohydride to yield 2-(benzyloxycarbonylamino)-2-deoxy-β-D-xylofuranoside (**3**). Selective esterification of **3** with *p*-toluenesulfonyl chloride in pyridine afforded, in 82% yield, benzyl 2-(benzyloxycarbonylamino)-2-deoxy-5-*O*-tosyl-β-D-xylofuranoside (**4a**), which was converted by partial hydrogenolysis with 10% Pd–C catalyst and subsequent *N*-acetylation into benzyl 2-acetamido-2-deoxy-5-*O*-tosyl-β-D-xylofuranose (**5**) in 96% yield. Glycoside **5** was treated with an excess of sodium azide in *N*,*N*-dimethylformamide for 4 h at 90°, to afford benzyl 2-acetamido-5-azido-2,5-dideoxy-β-D-xylofuranoside (**6**) in 92% yield. Acetylation of **6** with acetic anhydride in pyridine gave the crystalline 3-*O*-acetyl derivative (**7**).

The structure of **7** was determined by i.r. and n.m.r. spectroscopy: the presence of acetamido, azide, *O*-acetyl, and benzyl groups was shown by the i.r. spectrum, and the n.m.r. spectrum (of **7** in chloroform-*d*) revealed the presence of an acetamido and an *O*-acetyl group at δ 1.98 and 2.10, respectively, H-1 as a doublet at δ 5.12 (2.0 Hz), H-3 as a doublet of doublets due to couplings with H-2 and H-4 at δ 5.33 ($J_{2,3}$ 2.9, $J_{3,4}$ 6.7 Hz), NH at δ 6.35 (7.0 Hz), and phenyl protons at δ 7.37 (s, 5 H), and these data were consistent with structure **7**.

Hydrolytic removal of the benzyl group of **6** with 70:1 acetic acid–2M hydrochloric acid at 45°, and subsequent acetylation, afforded 2-acetamido-1,3-di-*O*-acetyl-5-azido-2,5-dideoxy-α-D-xylofuranose (**8b**). The n.m.r. spectrum of **8b** exhibited three singlets, integrating for nine protons, at δ 2.01, 2.06, and 2.08, which demonstrated the presence of one *N*-acetyl and two *O*-acetyl groups. A low-field doublet appearing at δ 6.40 (5.0 Hz) was assigned to the anomeric proton of the α-D-acetate; H-3 appeared at δ 5.55 (8.0 Hz) as a triplet due to coupling with H-2 and H-4, indicating a furanoid structure[8,10,11] having a 1-*O*-acetyl or 1-*O*-alkyl group cis to the group on C-2. On treatment with sodium methoxide in methanol, compound **8b** gave **8a**, which was used for the next reaction without purification. Compound **8a** reacted with 2,3-dihydro-4*H*-pyran in the presence of *p*-toluenesulfonic acid at room temperature, affording 2-acetamido-5-azido-2,5-dideoxy-1,3-di-*O*-(tetrahydropyran-2-yl)-α-D-xylofuranose (**9**) in 73% yield; significant signals in the n.m.r. spectrum were a one-proton doublet at δ 5.45 ($J_{1,2}$ 5.8 Hz, H-1), a three-proton singlet at δ 2.01 (AcN), and a high-field, twelve-proton multiplet at δ 1.34–1.88 (tetrahydro-

pyranyl methylene, C-CH_2-C). Other n.m.r. data are given in the Experimental section, and are consistent with structure **9**.

Reduction of the azide group in compound **9** (in 1,4-dioxane–triethylamine) with hydrogen in the presence of 10% Pd–C catalyst gave **10** quantitatively. Treatment of the amino compound **10** with sulfur dioxide in water for 4 min at 100°, according to a reported procedure[12], afforded, in good yield, the desired 2-acetamido-5-amino-2,5-dideoxy-D-xylopyranosyl hydrogensulfite (**11**). The i.r. and n.m.r. spectra were consistent with structure **11**. On the other hand, hydrogenation of **6** in the presence of 10% Pd–C catalyst afforded a *xylo*-piperidine derivative, well studied[13], which was isolated as the di-*N*-acetyl-di-*O*-acetyl derivative **12** by acetylation; the structure was supported by examination of the i.r. and n.m.r. spectra (see the Experimental section).



EXPERIMENTAL

General methods. — Melting points were determined on a Yanagimoto micro melting-point apparatus and are uncorrected. Specific rotations were determined with a Yanagimoto OR-50 polarimeter. N.m.r. spectra were recorded at 90 MHz with a Hitachi R-22 spectrometer. I.r. spectra were recorded with a Jasco IRA-1 spectrophotometer. Preparative chromatography was performed on 300-mesh silica gel (Waco Co.) with the solvent systems specified. Evaporations were conducted *in vacuo*.

Benzyl 2-(benzyloxycarbonylamino)-2-deoxy-β-D-glucofuranoside (**2**). — A solution of benzyl 2-(benzyloxycarbonylamino)-2-deoxy-5,6-*O*-isopropylidene-β-D-glucofuranoside[5] (**1**, 6.2 g) in 60% aqueous acetic acid (60 mL) was heated for 3 h at 40°, and then evaporated at 40°. The residue crystallized from ether, and recrystallization from ethanol–ether gave **2** as needles (4.4 g, 78%), m.p. 128°, $[\alpha]_D^{20}$

−35° (*c* 0.4, methanol); ν_{max}^{Nujol} 3400 (OH), 3300 (NH), 1680 and 1520 (amide), and 730 and 690 cm^{-1} (phenyl).

Anal. Calc. for $C_{21}H_{25}NO_7$: C, 62.52; H, 6.25; N, 3.47. Found: C, 62.48; H, 6.20; N, 3.38.

*Benzyl 2-(benzyloxycarbonylamino)-2-deoxy-β-*D*-xylofuranoside* (**3**). — To a solution of **2** (2.0 g) in methanol (50 mL) was added 0.2M aqueous sodium metaperiodate solution (32 mL) at 0°, and the mixture was kept for 2 h at 0°. In order to decompose the excess of the reagent, ethylene glycol was added to the mixture, and the precipitate was removed by filtration. The filtrate was evaporated to a syrup, which was extracted with chloroform. The extract was washed with water, dried (sodium sulfate), and evaporated to a syrup which was used in the next reaction without further purification. A solution of the syrup in methanol (50 mL) was stirred at 0° while sodium borohydride (55 mg) was added. The mixture was gently stirred for 3 h at 0°. Acetic acid (0.2 mL) was added to the mixture, and it was evaporated to a syrup which was extracted with chloroform. The extract was successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and evaporated, to afford a crystalline product; this was recrystallized from ethanol to give needles (1.54 g, 83%); m.p. 90–91°, $[\alpha]_D^{20}$ −59° (*c* 0.4, chloroform); ν_{max}^{Nujol} 3380 (OH), 3300 (NH), 1690 and 1535 (amide), and 710 and 680 cm^{-1} (phenyl).

Anal. Calc. for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21; N, 3.75. Found: C, 64.28; H, 6.19; N, 3.69.

*Benzyl 2-(benzyloxycarbonylamino)-2-deoxy-5-*O*-tosyl-β-*D*-xylofuranoside* (**4a**). — To an ice-cooled solution of **3** (2.0 g) in pyridine (20 mL) was added *p*-toluenesulfonyl chloride (1.2 g), and the mixture was kept for 5 h at room temperature. The mixture was evaporated, the residue extracted with chloroform, and the extract successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and evaporated to give a crystalline product. Recrystallization from ethanol afforded **4a** (2.3 g, 82%) as needles, m.p. 94–95°, $[\alpha]_D^{20}$ −46° (*c* 0.3, chloroform); ν_{max}^{Nujol} 3500–3300 (OH, NH), 1690 and 1500 (amide), 1180 (SO_2), and 730, 690, and 660 cm^{-1} (phenyl).

Anal. Calc. for $C_{27}H_{29}NO_8S$: C, 61.46; H, 5.54; N, 2.66. Found: C, 61.38; H, 5.46; N, 2.73.

*Benzyl 3-*O*-acetyl-2-(benzyloxycarbonylamino)-2-deoxy-5-*O*-tosyl-β-*D*-xylofuranoside* (**4b**). — Compound **4a** (100 mg) was acetylated with acetic anhydride–pyridine for 3 h at 45°, and the product was recrystallized from ethanol–ether to give 90 mg (83%) of **4b**, m.p. 99–100°, $[\alpha]_D^{20}$ −39°; ν_{max}^{Nujol} 3300 (NH), 1750 and 1230 (ester), 1720 and 1530 (amide), 1180 (SO_2), and 740, 700, and 660 cm^{-1} (phenyl); n.m.r. data (in chloroform-*d*): δ 2.00 (s, 3 H, AcO), 2.39 (s, 3 H, MeAr), 4.10–4.79 (m, 6 H, H-2,4,5,5′, benzyl methylene), 5.04 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 5.10 (s, 2 H, CO_2CH_2Ph), 5.32 (d of d, 1 H, $J_{2,3}$ 2.0, $J_{3,4}$ 6.0 Hz, H-3), and 7.26–7.88 (m, 15 H, NH, aromatic protons).

Anal. Calc. for $C_{29}H_{31}NO_9S$: C, 61.15; H, 5.49; N, 2.46. Found: C, 61.21; H, 5.60; N, 2.45.

Benzyl 2-acetamido-2-deoxy-5-O-tosyl-β-D-xylofuranoside (**5**). — Compound **4a** (2.5 g) was dissolved in 1,4-dioxane (20 mL); 10% Pd–C catalyst (250 mg) was added, and hydrogen was bubbled through the mixture, with stirring, for 2 h at room temperature. The catalyst was removed by filtration, and the filtrate was evaporated. To a solution of the amino compound in methanol (20 mL) was added acetic anhydride (4 mL), and, after 10 min, the mixture was evaporated, to give a crystalline mass which was recrystallized from ethanol–ether. Compound **5** was obtained as needles, 1.98 g (96%), m.p. 125°, $[\alpha]_D^{20}$ −53° (*c* 0.3, chloroform); ν_{max}^{Nujol} 3450–3400 (OH, NH), 1640 and 1550 (amide), 1180 (SO_2), and 730, 690, and 660 cm^{-1} (phenyl).

Anal. Calc. for $C_{21}H_{25}NO_7S$: C, 57.92; H, 5.79; N, 3.22. Found: C, 57.55; H, 5.63; N, 3.21.

Benzyl 2-acetamido-5-azido-2,5-dideoxy-β-D-xylofuranoside (**6**). — To a solution of **5** (580 mg) in dry *N*,*N*-dimethylformamide (5 mL) was added sodium azide (200 mg), and the mixture was heated with stirring for 4 h at 90°, evaporated, and extracted with chloroform. The extract was successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and evaporated to give a crystalline mass. Recrystallization from ether–hexane afforded **6** (380 mg, 92%) as needles, m.p. 161–162°, $[\alpha]_D^{20}$ −33° (*c* 0.3, chloroform); ν_{max}^{Nujol} 3440 (OH), 3280 (NH), 2080 (azide), 1660 and 1560 (amide), and 750 and 690 cm^{-1} (phenyl).

Anal. Calc. for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92; N, 18.29. Found: C, 54.80; H, 5.89; N, 18.51.

Benzyl 2-acetamido-3-O-acetyl-5-azido-2,5-dideoxy-β-D-xylofuranoside (**7**). — Compound **6** (150 mg) was acetylated with acetic anhydride–pyridine for 2.5 h at 50°, to give 140 mg (82%) of a product having m.p. 104–105°, $[\alpha]_D^{20}$ −61° (*c* 0.3, chloroform); ν_{max}^{Nujol} 3240 (NH), 2060 (azide), 1730 and 1220 (ester), 1640 and 1550 (amide), and 740 and 680 cm^{-1} (phenyl); n.m.r. data (in chloroform-*d*): δ 1.98, 2.10 (2 s, 6 H, AcN, AcO), 3.25–3.78 (m, 2 H, H-5,5′), 4.21–4.98 (m, 4 H, H-2,4, benzyl methylene), 5.12 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 5.33 (d of d, 1 H, $J_{2,3}$ 2.9, $J_{3,4}$ 6.7 Hz, H-3), 6.35 (d, 1 H, $J_{2,NH}$ 7.0 Hz, NH), and 7.37 (s, 5 H, Ph).

Anal. Calc. for $C_{16}H_{20}N_4O_5$: C, 55.16; H, 5.79; N, 16.08. Found: C, 55.09; H, 5.88; N, 16.13.

2-Acetamido-5-azido-2,5-dideoxy-1,3-di-O-(tetrahydropyran-2-yl)-α-D-xylofuranose (**9**). — To a solution of **6** (3.0 g) in acetic acid (70 mL) was added 2M hydrochloric acid (1.0 mL). The mixture was heated for 3 h at 45°, and then cooled, and treated with Amberlite IR-45 ion-exchange resin; the resin was filtered off and washed with acetic acid. The filtrate and washings were combined, and evaporated at 45°. The residue was acetylated with acetic anhydride–pyridine, and the product was chromatographed on a column of silica gel (100 g) with chloroform, and then with 50:1 chloroform–methanol. The latter eluate yielded the α anomer of **8b** (1.8 g, 61%) as a syrup; ν_{max}^{film} 3260 (NH), 2070 (azide), 1750 and 1220 (ester), and 1650 and 1540 cm^{-1} (amide); n.m.r. data (in chloroform-*d*): δ 2.01, 2.06, 2.08 (3 s, 9 H, AcN, 2 AcO), 3.43–3.51 (m, 2 H, H-5,5′), 4.37–5.02 (m, 2 H, H-2,4), 5.55 (t, 1 H, $J_{2,3} = J_{3,4} = 8.0$ Hz, H-3), 6.24 (d, 1 H, $J_{2,NH}$ 7.0 Hz, NH), and 6.40 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1).

Compound **8b** (1.5 g) was dissolved in methanol (100 mL), and sodium metal (10 mg) was added; after being kept for 10 min, the mixture was treated with Amberlite IRC-50 ion-exchange resin. After removal of the resin, the solution was evaporated, to give a syrup of **8a**, which showed a single spot in t.l.c. To a stirred solution of **8a** in 1,4-dioxane (50 mL) were added 2,3-dihydro-4*H*-pyran (2.0 mL) and *p*-toluenesulfonic acid monohydrate (100 mg). The mixture was stirred at room temperature while the progress of the reaction was monitored by t.l.c.; after 24 h, the starting material and mono-*O*-tetrahydropyran-2-yl derivative were no longer detectable. The mixture was treated with Amberlite IRA-410 (OH^-) ion-exchange resin to remove the acid, and evaporated to a syrup. The product was chromatographed on a column of silica gel (30 g) with chloroform, and then with 200:1 chloroform–methanol. The latter eluate yielded compound **9** (1.55 g, 73%) as a syrup, $[\alpha]_D^{20}$ +49° (*c* 0.5, chloroform); ν_{max}^{film} 3290 (NH), 2090 (azide), and 1650 and 1540 cm^{-1} (amide); n.m.r. data (in chloroform-*d*): δ 1.34–1.88 (m, 12 H, tetrahydropyranyl methylene, C-CH_2-C), 2.01 (s, 3 H, AcN), 3.40–3.92 (m, 6 H, H-5,5′, tetrahydropyranyl methylene, O-CH_2-C), 4.22–4.43 (m, 2 H, H-3,4), 4.60 (m, 1 H, H-2), 4.80–5.04 (m, 2 H, tetrahydropyranyl methyne), 5.45 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), and 6.2 (d, 1 H, $J_{2,NH}$ 8.0 Hz, NH).

Anal. Calc. for $C_{17}H_{28}N_4O_6$: C, 53.11; H, 7.34; N, 14.58. Found: C, 53.34; H, 7.58; N, 14.29.

2-Acetamido-5-amino-2,5-dideoxy-1,3-di-O-(*tetrahydropyran-2-yl*)-α-D-*xylofuranose* (**10**). — A solution of **9** (650 mg) in 1,4-dioxane (100 mL) and triethylamine (20 mL) was hydrogenated in the presence of 10% Pd–C catalyst (200 mg) for 1.5 h; at this time, t.l.c. showed the reaction to be complete. The suspension was filtered, and the filtrate was evaporated to a syrup which was chromatographed on a column of silica gel (20 g) with 50:1 chloroform–methanol. The amino compound **10** (600 mg, quantitative yield) was obtained as a syrup, $[\alpha]_D^{20}$ +28° (*c* 0.5, methanol); ν_{max}^{film} 3380 (NH), and 1650 and 1540 cm^{-1} (amide).

Anal. Calc. for $C_{17}H_{30}N_2O_6$: C, 56.96; H, 8.44; N, 7.82. Found: C, 56.88; H, 8.65; N, 7.58.

2-Acetamido-5-amino-2,5-dideoxy-D-*xylopyranosyl hydrogensulfite* (**11**). — Compound **10** (100 mg) was dissolved in water (6 mL), and sulfur dioxide was vigorously bubbled through the solution for 30 min at 0°. The reaction vessel was sealed, and it was kept for 10 h at room temperature. The mixture was evaporated at 30°, to give a crystalline mass which was dissolved in water (4 mL). The solution was heated for 4 min at 100°, and evaporated at 30° to give a crystalline mass. Recrystallization from water–acetone gave needles of **11** (55 mg, 82%), m.p. 200–208° (dec.), $[\alpha]_D^{20}$ +9.3° (*c* 0.3, water); ν_{max}^{Nujol} 3400–3200 (OH, NH), 1650 and 1540 (amide), and 1170 cm^{-1} (SO_2); n.m.r. data (D_2O): δ 1.86 (s, 3 H, AcN), 3.20–3.33 (m, 2 H, H-5,5′), 3.50–3.75 (m, 1 H, H-4), 4.35–4.63 (m, H-1β,2,3) and 5.29 (d, $J_{1,2}$ 4.0 Hz, H-1α).

Anal. Calc. for $C_7H_{14}N_2O_6S$: C, 33.06; H, 5.55; N, 11.02. Found: C, 33.34; H, 5.47; N, 11.16.

3-Acetamido-4,5-diacetoxy-1-acetyl-xylo-*piperidine* (**12**). — A solution of **6** (300 mg) in ethanol (40 mL) was hydrogenated in the presence of 10% Pd–C catalyst (200 mg) for 1 h. After removal of the catalyst by filtration, acetic acid (1 mL) was added to the filtrate, and the mixture was evaporated at 40° to give a crystalline mass. The amino compound was dissolved in 9:1 methanol–water (30 mL); 10% Pd–C catalyst (200 mg) was added, and hydrogen was again bubbled through for 1 h at 35°, the course of the reaction being monitored by t.l.c. The catalyst was filtered off, and the filtrate was evaporated to a syrup which was acetylated with acetic anhydride (2 mL) in pyridine (10 mL). The product was purified by chromatography on a column of silica gel (15 g) with chloroform, and then with 30:1 chloroform–methanol. The latter eluate gave **12** (230 mg, 78%), m.p. 67–69°, $[\alpha]_D^{20}$ −15° (*c* 0.7, ethanol); ν_{max}^{Nujol} 3250 (NH), 1745 and 1240 (ester), and 1650 and 1540 cm^{-1} (amide); n.m.r. data (in chloroform-*d*): δ 1.93, 2.02, 2.09 (s, 2 s, s, 12 H, 2 AcO, 2 AcN), 2.75–4.05 (m, 4 H, H-2,6,2′,6′), 4.13–4.49 (m, 1 H, H-3), 4.68–5.10 (m, 2 H, H-4,5), and 6.45–6.65 (near d, 1 H, NH); (in methanol-d_4): δ 1.91, 2.00, 2.12 (s, 2 s, s, 12 H, 2 AcO, 2 AcN), 2.60–4.05 (m, 4 H, H-2,6,2′,6′), 4.12–4.95 (m, 2 H, H-3,5), and 5.08 (t, 1 H, $J_{3,4} = J_{4,5} = 9.0$ Hz, H-4).

Anal. Calc. for $C_{13}H_{20}N_2O_6$: C, 51.99; H, 6.71; N, 9.33. Found: C, 51.86; H, 6.59; N, 9.31.

REFERENCES

1 A. HASEGAWA, E. TANAHASHI, AND M. KISO, *Gifu Daigaku Nogakubu Kenkyu Hokoku*, 41 (1978) 133–138.
2 H. PAULSEN, *Angew. Chem.*, 78 (1966) 501–556.
3 R. L. WHISTLER AND A. K. M. ANISUZZAMAN, *A.C.S. Symp. Ser.*, 39 (1976) 133–154.
4 A. HASEGAWA AND H. G. FLETCHER, JR., *Carbohydr. Res.*, 29 (1973) 223–237.
5 A. HASEGAWA, T. SAKURAI, AND N. HASEGAWA, *Carbohydr. Res.*, 45 (1975) 19–27.
6 A. HASEGAWA, N. ARITAKE, AND M. KISO, *Carbohydr. Res.*, 51 (1976) c10–c12.
7 A. HASEGAWA, N. ARITAKE, AND M. KISO, *Carbohydr. Res.*, 52 (1976) 137–149.
8 A. HASEGAWA, Y. KAWAI, H. KASUGAI, AND M. KISO, *Carbohydr. Res.*, 64 (1978) 131–137.
9 A. HASEGAWA, T. SAKURAI, AND M. KISO, *Agric. Biol. Chem.*, 42 (1978) 153–158.
10 A. HASEGAWA AND M. KISO, *Carbohydr. Res.*, 63 (1978) 91–98.
11 B. L. KAM, J.-L. BARASCUT, AND J.-L. IMBACH, *Carbohydr. Res.*, 69 (1979) 135–142.
12 H. PAULSEN, F. LEUPOLD, AND K. TODT, *Chem. Ber.*, 99 (1966) 200–214.
13 S. INOUE, T. TSURUOKA, T. ITO, AND T. NIIDA, *Tetrahedron*, 24 (1968) 2125–2144.