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<td>Author(s)</td>
<td>吉村 寿次; YOSHIMURA, Juji; 佐藤 憲一; SATO, Kenichi; 橋本 弘信; HASHIMOTO, Hironobu; SHIMIZU, Kuniaki</td>
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Aminosugars. XXVIII. A Facile Synthesis of Benzyl α- and β-Kasugaminides via the Corresponding Abequosides

Juji Yoshimura, Ken-ichi Sato, Hironobu Hashimoto, and Kuniiaki Shimizu

Laboratory of Chemistry for Natural Products, Faculty of Science, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

(Received April 19, 1977)

Synthesis of benzyl α- and β-kasugaminides (benzyl 2,4-diamino-2,3,4,6-tetraideoxy-α- and β-D-xylo-hexopyranosides) was carried out by the simultaneous substitution at 2,4-positions of 2,4-di-O-mesy1-abequosides (3,6-dideoxy-2,4-di-O-mesy1-α- and β-D-xylo-hexopyranosides) with sodium azide followed by hydrogenation. The substitution in N,N-dimethy1formamidine at higher temperature gave the elimination products (4-azido-2,3-unsaturated derivatives) and the subsequently rearranged products (3,4-unsaturated 2-azido derivatives), but, that in hexamethy1phosphor0triamide at lower temperature gave the desired compounds in fairly good yields.

In connection with synthetic studies on kasugamycin \(^3\,^9\) and optically active \(^6\) methyl α-kasugamidine (methyl 2,4-diamino-2,3,4,6-tetraideoxy-α-D-arabino-hexopyranoside) have been published. The necessity of the resolution of a racemate is a shortcoming in the former synthesis, whereas the stepwise conversion in the latter takes longer steps, and consequently gives a lower overall yield.

In order to study the relationship between the configuration of aminosugar moiety in kasugamycin and the biological activity, we intended to develop a better pathway for synthesis of optically active kasugamidine and its diastereomers. In this paper, a facile synthesis of benzyl α- and β-kasugaminides via the simultaneous α-β-substitution at 2,4-positions of the corresponding akequosides (benzyl 3,6-dideoxy-α- and β-D-xylo-hexopyranosides) is described. As methyl α-abequoside \(^7\,^9\) is known to be synthesized by the simultaneous deoxygenation of 3,6-positions of methyl 3,4-anhydro-6-O-p-tolylsulfonyl-α-D-galactopyranoside obtainable from d-glucose, the pathway offered here is advantageous.

Results and Discussion

According to the method of Siewert and Westphal \(^7\), benzyl α- and β-abequosides were newly prepared. Benzoylation of benzyl 4,6-O-benzyldiene-α- \(^10\) and β-D-glucopyranosides \(^11\) in the usual manner gave the 2,3-di-O-benzoates \((1x) and \((1β) in good yields, respectively. Partial hydrolysis of the 4,6-O-benzyldiene group in \(1x\) and \(1β\) proceeded quantitatively in 70% acetic acid at 90—95°C to give \(2x\) and \(2β\), respectively. Mesylation of \(2x\) and \(2β\) in the usual manner gave the corresponding 4,6-di-O-mesy1ates \((3x) and \(3β) in good yields, respectively. Benzyl 2,3-di-O-benzoyl-4,6-di-O-p-tolylsulfonyl-β-D-glucopyranoside \((4) was also prepared from \(2β\) in a similar manner.

Examination of the conversion of \(3β\) in dichloromethane or chloroform into the corresponding epoxide \((7β) by treatment with sodium methoxide in methanol indicated that \(3β\) was once changed into an intermediate \((5) within 5 h and then gradually converted into \(7β\).

In fact, \(5\) deposited from the reaction mixture, when the amount of solvents (especially methanol) was not enough. This conversion proceeded slower than that of the corresponding methyl glucoside \(^7\) and the use of a little excess (1.3—1.4 mol) sodium methoxide gave a better result. Thus, \(7α\) and \(7β\) were obtained in 64 and 75% yields, respectively. In a similar way, tosylated intermediate \((6) and tosylated epoxide \((8) were obtained from \(4\). It was characteristic that NMR spectra of these epoxides showed a coupling between OH and H, and a AB-quartet of H and H. Reduction of \(7α\), \(7β\), and \(8\) in tetrahydrofuran (THF) with 3 mol of lithium aluminium hydride (LAH) gave sirupy benzyl akequosides \((9α\) and \(9β) respectively. When 1.5 mol of LAH were used in one instance, crystalline benzyl 3-deoxy-β-D-xylo-hexopyranoside \((10) was separated on a silica gel column in 22% yield, indicating that the epoxide ring was more reducible than the 6-O-sulfonate group. Excepting the last step in the synthesis of \(9α\) and \(9β\), the purification of the product in each reaction was not always necessary, and both α- and β-abequosides could be actually obtained in ca. 20% overall yield from D-glucose. Mesylation of \(9α\) or \(9β\) and \(10\) gave the corresponding 2,4-di-O-mesy1ates \((11α) or \(11β) and 2,4,6-tri-O-mesy1ate \((12) in good yields, respectively.
The simultaneous substitution at 2,4-positions of mesylates mentioned above with sodium azide was unexpectedly accompanied with the formation of unsaturated products. Reaction of 11β in N,N-dimethylformamide (DMF) with 3 mol of sodium azide at 120 °C overnight was incomplete, and two spots other than a small amount of the starting material were detected on TLC. Separation of the products on a silica gel column gave one monoazide (14β) in pure state, but the NMR spectrum of another fraction indicated the presence of unsaturated compounds. Reaction of 12 under the same condition gave also the corresponding 4,6-diazide (15) in a low yield. Even after the reaction of 11β was continued at 160—165 °C until 14β disappeared, the mixture of products could not be separated by repeating column chromatography. Therefore, the separation was tried after hydrogenation of the products with LAH in THF followed by N-acetylation. Thus, benzyl N,N-diacetyl-β-kasugamimide (16β) and benzyl 4-acetamido-2,3,4,6-tetrahydroxy-β-D-erythro-hex-2-enopyranoside (17) could be isolated in 12 and 19% yields, respectively. When the hydrogenation was carried out in the presence of Raney nickel, the corresponding saturated amino derivatives could be separated by column chromatography into three sirupy products (19, 20, and 18) in 8, 19, and 42% yields, respectively. These compounds were characterized after quantitative conversion into N-acetyl derivatives (21, 22, and 16β). The first-order analysis of the NMR spectrum of 16β (cf. Experimental) completely proved the allocated structure, and \( J_{3,2} \) values of 21 (\( J_{3,2}=2.4 \)) and 22 (\( J_{3,2}=8.2 \)) supported them. It will be noteworthy that 19 is a glycoside of the enantiomer of natural L-tolypos-amine,12,13)

The results mentioned above suggest that the second substitution at C-2 of the initial product (14β) gives 2,4-diazide (13β), but the substitution is followed by the elimination of axial C-2-azido group to give benzyl 4-azido-2,3,4,6-tetrahydroxy-β-D-erythro-hex-2-enopyranoside (23), which subsequently rearranges to the corresponding 2-azido-3-enopyranoside (24). Recently, several papers have been published on the thermal rearrangement of 2,3-unsubstituted 4-azido- and 4-thiocyanatoglycopyranosides to 3,4-unsubstituted sugars having nitrogen function at C-2.14–10) These conversions were explained as a [3,3]-sigmatropic rearrangement of cyclic allylic systems in which the asymmetry at the initial allylic centre is transmitted to the new centre by the suprafacial migration.14) Although the formation of a small amount of unsaturated product in the substitution of equatorial C4-sulfonyloxy group attached to 3-deoxy-hexopyranoside-ring with sodium azide in DMF has been reported,15) the question whether the formation of 23 is initiated from the equatorial C4-sulfonyloxy group of 14β or from axial C4-azido group of 13β was remained ambiguous.

In order to prevent the formation of unsaturated compounds, the same substitution of 11α and 11β was examined at a lower temperature, using hexamethylenephosphoric triamide (HMPA) as a solvent. As shown in Table 1, the reaction at 80 °C gave exclusively monosubstituted 14 in good yields. The continuation of the reaction at 120 °C until 14 disappeared also resulted in the formation of unsaturated compounds, but the yields of the desired diazides (13) were improved. Actually, 16α and 16β were obtained from the crude products in 60 and 46% yields, respectively, by subsequent hydrogenation and N-acetylation. The structure of 16β and 16β was further confirmed by respective hydrogenation into known N,N'-diacetyl-kasugamine (25).16) It has been reported that the substitution of methyl 4,6-O-isopropylidene-3-O-methyl-2-O-methyl-sulfonfyl-β-D-gluco- and β-mannopyranoside with potassium benzoate in DMF proceeded smoothly, whereas that of α-anomers did not occur.18) Slower but steady substitution of the α-anomer in this experiment will be attributed to the absence of substituent at C-3 and to the flexibility of 11α.

<table>
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<tr>
<th>Conditions</th>
<th>Products (%)</th>
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<tr>
<td>Temp (°C)</td>
<td>Time (h)</td>
</tr>
<tr>
<td>11α</td>
<td>80</td>
</tr>
<tr>
<td>11α</td>
<td>120</td>
</tr>
<tr>
<td>11β</td>
<td>80</td>
</tr>
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<td>11β</td>
<td>100</td>
</tr>
<tr>
<td>11β</td>
<td>120</td>
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a) Yields were estimated from the weight of crude products and the intensity ratio of olefinic proton and others in NMR spectra.
**Experimental**

All melting points are uncorrected. The solutions were evaporated under diminished pressure at a bath temperature not exceeding 45°C. Specific rotations were measured in a 0.5-dm tube, with a Carl Zeiss LEP-Al polarimeter. The IR spectra were recorded with a Hitachi Model EPI-G2 spectrometer. The NMR spectra were taken with a JEOL-4H-100 MHz spectrometer using tetramethylsilane as an internal standard, in deuteriochloroform unless otherwise stated. Chemical shifts and coupling constants were recorded in δ and Hz units, and IR frequencies in cm⁻¹.

**Benzy 2,3-Di-O-benzoyl-4,6-O-benzylidene-α- and β-D-glucopyranosides (1a and 1b).**

Benzyl 4,6-O-benzylidene-β-D-glucopyranoside (2) was benzoylated with benzoyl chloride in benzene. A usual work up and recrystallization of the product from ethanol gave pure 1a in 95% yield. Mp 167–168.5°C; [α]D20 = -19.0° (c 0.5, CHCl₃). IR: 1728 (ester), 1600 (Ph), NMR: 7.95 and 7.60–7.00 (Ph; m), 5.73 (H₂; t, J₂,₃ = 9.2), 5.52 (H₁; q, J₁,₂ = 8.8), 5.51 (CH: s), 4.79 (H3; d, J₃,₄ = 7.4), 4.87 and 4.62 (CH₂; ABq, J₂,₃ = 12.5), 4.41 (H₄; q, J₄,₅ = 10.0), 3.93 (H₁; t, J₁,₂ = 8.8), 3.87 (H₂; t, J₂,₃ = 8.6), 3.72 (H₃; m, J₃,₄ = 5.0). Found: C, 72.02; H, 5.34%. Calcd for C₂₆H₂₇O₇: C, 72.07; H, 5.34%.

Similarly, benzoylation of benzyl 4,6-O-benzylidene-α-D-glucopyranoside (2) gave 1a in 95% yield. Mp 134–136°C; [α]D20 = +123.2° (c 0.35, CHCl₃). IR: 1700 (ester), 1600 (Ph); NMR: 7.75 and 7.50–7.10 (Ph; m), 6.10 (H₂; t, J₂,₃ = 9.3), 5.51 (CH: s), 5.28 (H₁; broad s), 5.23 (H₁; q, J₁,₂ = 3.5), 4.72 and 4.53 (CH₂; ABq, J₂,₃ = 13.0), 4.35–3.70 (H₃, H₄, and H₅). Found: C, 72.34; H, 5.34%. Calcd for C₂₅H₂₆O₇: C, 72.07; H, 5.34%.

A suspension of 2 (30 g) in 70% acetic acid in 90% yield. Mp 165-166°C; [α]D20 = -108.3° (c 1.0, CHCl₃). IR: 3400 (OH), 1490 (Ph), 1350 and 1190 (sulfate); NMR: 7.30 (Ph; s), 4.80 and 4.53 (CH₂; ABq, J₂,₃ = 11.5), 4.42–4.30 (H₄ and H₅; m), 4.22 (H₂; d, J₂,₃ = 7.0), 4.19 (H₃; t, J₃,₄ = 5.7), 3.68 (H₂; q, J₂,₃ = 3.8), 3.21 and 3.12 (H₄ and H₅; each d, J₄,₅ = 3.8), 2.99 (OSO₂CH₃), 2.66 (OH; d). Found: C, 51.38; H, 5.42; S, 9.41%. Calcd for C₂₃H₂₆O₇S: C, 50.90; H, 5.49; S, 9.71%.

When the amount of solvents or the reaction time in the above reaction was not enough, the intermediate, benzyl 4,6-di-O-methylsulfonfyl-β-D-glucopyranoside (5) deposited from the reaction mixture or from the chloroform layer during the washing with water. It was characterized as follows: mp 101–103°C; [α]D20 = -41.8° (c 0.86, MeOH); IR: 3400 (OH), 1490 (Ph), 1350 and 1190 (sulfate). Found: C, 42.12; H, 5.39; S, 14.74%. Calcd for C₂₃H₂₆O₇S: C, 42.24; H, 5.20; S, 15.04%.

Similarly, 3a was converted into 7a in 64% yield. Mp 73–74°C (from ethanol-hexane); [α]D20 = +42.4° (c 0.5, CHCl₃). IR: 3350 (OH), 1495 (Ph), 1350 and 1190 (sulfate); NMR: 7.40 (Ph, s), 4.94 (H₁; d, J₁,₂ = 4.8), 4.84 and 4.60 (CH₂; ABq, J₂,₃ = 11.5), 4.45–4.30 (H₄ and H₅; m), 3.85 (H₂; q, J₂,₃ = 10.5), 3.30 and 3.24 (H₄ and H₅; ABq, J₂,₃ = 2.6), 3.07 (OSO₂CH₃), 2.50 (OH; d). Found: C, 50.02; H, 5.56; S, 9.39%. Calcd for C₂₇H₂₆O₇S: C, 50.90; H, 5.49; S, 9.71%.

**Benzy 3,4-Anhydro-6-O-methylsulfonfyl-α- and β-D-glucopyranosides (7a and 7b).**

A solution of 3 (14.8 g, 124 mmol) in chloroform (150 ml) was added a methanol solution (100 ml) of sodium methoxide (0.56 g, 12 equiv. of sodium) and then kept in a refrigerator overnight. The reaction mixture was diluted with chloroform (100 ml), and then washed three times with water. The chloroform layer was dried and evaporated to give a sirup which was crystallized from benzene–petroleum ether. Yield 5.8 g (75%); mp 77–78°C; [α]D20 = -108.3° (c 1.0, CHCl₃). IR: 3400 (OH), 1490 (Ph), 1350 and 1190 (sulfate); NMR: 7.30 (Ph; s), 4.80 and 4.53 (CH₂; ABq, J₂,₃ = 11.5), 4.42–4.30 (H₄ and H₅; m), 4.22 (H₂; d, J₂,₃ = 7.0), 4.19 (H₃; t, J₃,₄ = 5.7), 3.68 (H₂; q, J₂,₃ = 3.8), 3.21 and 3.12 (H₄ and H₅; each d, J₄,₅ = 3.8), 2.99 (OSO₂CH₃), 2.66 (OH; d). Found: C, 51.38; H, 5.42; S, 9.41%. Calcd for C₂₃H₂₆O₇S: C, 50.90; H, 5.49; S, 9.71%.
washed, and the residue was dissolved in water. Sodium periodate (2 g, 7.5 mmol) was added to the aqueous solution and kept in a refrigerator overnight. After addition of hydrogen peroxide (30%), the mixture was reduced with excess sodium thiosulfate, evaporated, and an aqueous solution of the residue was extracted with chloroform.

Evaporation of the extracts gave a sirup (3.8 g) which was fractionated on silica gel column (eluant: benzene=1:9) to give pure 9a (3.0 g, 52%) as a sirup, [α]D = −107° (c 0.5, CHCl3).

Found: C 65.61; H, 7.72%. Calcd for C13H23O5S: C, 65.53; H, 7.61%.

The same compound was also obtained from 8 in 48.5% yield.

In a similar manner mentioned above, 9a was obtained from 7a in 53% yield as a sirup, [α]D = +119° (c 0.8, CHCl3).

Found: C 64.98; H, 7.38%. Calcd for C13H23O5S: C, 65.55; H, 7.61%.

In case of 1.5 mol of LAH were used for hydrogenation of 7a, fractionation of the product gave benzyl 3-deoxy-β-D-xyl-hexopyranoside (11β) in 22% yield. Mp 95—95.5°C; [α]D = −59.0° (c 1.1, MeOH).

Found: C 61.17; H, 7.08%. Calcd for C13H23O5S: C, 61.40; H, 7.14%.

Benzyl 3,6-Dideoxy-2,3,6-tri-O-methylsulfonyl-β-D-xylo-hexopyranoside (11α and 11β).

Mesylation of 9β in the usual manner, and crystallization of the product from ethanol gave 11β in 77% yield. Mp 104—105°C; [α]D = −64° (c 1.0, CHCl3).

IR: 3400 (OH), 1665 (C=O); NMR: 7.35 (Ph, s), 4.92 and 4.39 (CH2: Abq: J.6=12.6), 4.23 (H2: m), 4.68—4.70 (H2: m), 4.50 (H2: m), 4.40—4.45 (H2: m), 3.80 (H6: octet, J.7=1.5), 2.91 and 3.08 (2×OSO2CH2), 2.71 (H2: m, J.7=12.7), 2.04 (H: m), 1.35 (CH3: d). Found: C, 45.91; H, 5.68; S, 16.28%. Calcd for C25H30O15S: C, 45.67; H, 5.62; S, 16.26%.

Similarly, 9a was mesylated to give 11α quantitatively. Mp 92—93°C (from ethanol–hexane); [α]D = −95.2° (c 0.6, CHCl3).

IR: 3400 (OH), 1540 and 1175 (sulfate); NMR: C 45.86; H, 5.63; S, 16.31%. Calcd for C25H30O15S: C, 45.67; H, 5.62; S, 16.26%.

Benzyl 3-Deoxy-2,3,6-tri-O-methylsulfonyl-β-D-xylo-hexopyranoside (12).

Mesylation of 10 in pyridine with methanesulfonyl chloride gave the tri-O-mesylate in 76% yield. Mp 123—126°C; [α]D = −59.6° (c 1.0, CHCl3); IR: 1350 and 1180 (sulfate); NMR: 7.32 (Ph, s), 4.90 and 4.90 (H2: m), 4.65 (H2: m), 4.40—4.45 (H2: m), 3.80 (H6: octet, J.7=1.5), 2.91 and 3.08 (2×OSO2CH2), 2.71 (H2: m, J.7=12.7), 2.04 (H: m), 1.35 (CH3: d). Found: C, 45.91; H, 5.68; S, 16.28%. Calcd for C25H30O15S: C, 45.67; H, 5.62; S, 16.26%.

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A Facile Synthesis of Kasugaminides via Abequosides

December, 1977

A. K. Al-Radhi, K. Maeda, H. Umezawa, and M. Ohno,

The preparation of benzyl-β-kasugaminide (18), benzyl-α,β-amino-2,3,4,6-tetrahydroxy-β-D-erythro-hexopyranoside (19), benzyl-α-amino-2,3,4,6-tetrahydroxy-β-D-erythro-hexopyranoside (20), and their conversion into the corresponding N-acetates (16β, 19, and 22) was described.

In the same manner mentioned above, the reaction of 11β (7.5 g) with sodium azide was carried out, and the crude product was hydrogenated in the presence of Raney nickel at 50°C for 5 h under 50 atm hydrogen gas to give a sirup which showed three spots on TLC. The sirup on a silica gel (60 g Wakogel C-200) column was eluted with benzene-ether-chloroform (1:1:0.1, 10 ml), 5:1 (500 ml), and 1:1 (5 ml) to give 20 (0.8 g, 19.0%), 19 (0.34 g, 8.1%), and 18 (1.82 g, 41.9%) as a sirup, respectively. Each sirup was acetylated with acetic anhydride and pyridine. The reaction mixture was directly evaporated to dryness, and the product was purified by column chromatography if necessary. Each acetate obtained in almost quantitative yield was characterized with NMR spectrum, respectively.

Compound 20 was not characterized.

17: Mp 162-164°C; [a]D25 = -249° (c 0.2, CHCl₃); IR: 3270 (NH), 1640 and 1550 (amide); NMR: 7.35 (Ph, s), 4.90 and 4.58 (CH₂: ABq, J₆,7 = 12.0), 4.36 (H₂: d, J₆,₇ = 8.2), 3.82-3.40 (H₂ and H₆: m), 2.3-1.3 (H₃a, H₄a, H₆a, and H₄m: m), 1.90 (NAc), 1.26 (CH₃: d, JCH₃,D = 6.5). Found: C, 68.72; H, 8.30; N, 5.60%. Calcd for C₁₆H₂₁NO₅: C, 68.27; H, 8.13; N, 5.51%.

18: [a]D25 = -70.8° (c 1.1, CHCl₃). Found: C, 69.95; H, 8.88; N, 6.32%. Calcd for C₁₆H₂₁NO₅: C, 70.55; H, 8.65; N, 6.33%.

19: [a]D25 = -90.4° (c 0.6, CHCl₃); IR: 3280 (NH), 1635 and 1550 (amide); NMR: 7.35 (Ph, s), 4.88 and 4.58 (CH₂: ABq, J₆,7 = 12.0), 4.36 (H₂: d, J₆,₇ = 8.2), 3.82-3.40 (H₂ and H₆: m), 2.3-1.3 (H₃a, H₄a, H₆a, and H₄m: m), 1.90 (NAc), 1.26 (CH₃: d, JCH₃,D = 6.5). Found: C, 68.72; H, 8.30; N, 5.60%. Calcd for C₁₆H₂₁NO₅: C, 68.27; H, 8.13; N, 5.51%.

16β: mp 164-166°C; [α]D25 = -98.8° (c 0.5, CHCl₃); IR: 3270 (NH), 1635 and 1545 (amide); NMR: 7.35 (Ph, s), 4.90 and 4.58 (CH₂: ABq, J₆,7 = 12.0), 4.36 (H₂: d, J₆,₇ = 8.2), 3.70 (H₂: d₃, J₆,₇ = 10.0, J₆,₅ = 4.4), 3.36 (H₂: dq, J₅,₆ = 6.0), 1.98 (NAc), 2.22-1.38 (H₃a, H₄a, H₆a, and H₄m: m). Found: C, 68.82; H, 8.20; N, 5.57%. Calcd for C₁₆H₂₁NO₅: C, 68.41; H, 8.04; N, 5.52%.

Benzyl 2,4-disaccharide of 18 was obtained in almost the same yield as 18.

References


