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Saponin and Sapogenol. XXVIII.[1] Reinvestigation of the Branching Positions in the Glucuronide Moieties of Three Glucuronide Saponins: Desacyl-jegosaponin, Desacyl-boninsaponin A, and Sakuraso-saponin

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The branching positions in the glucuronide moieties of desacyl-jegosaponin (**1**), desacyl-boninsaponin A (**2**), and sakuraso-saponin (3) have been reinvestigated. It has been found that the branching positions in the glucuronide moieties of these glucuronide saponins should be revised to C-2 and C-3 from the previously assigned C-2 and C-4.

Keywords——glucuronide saponin; desacyl-jegosaponin; desacyl-boninsaponin A; sakuraso-saponin; methylated monosaccharide; GLC; TLC

Several years ago, we reported the structures of three glucuronide saponins: desacyl-jegosaponin from the pericarps of *Styrax japonica* Sieb. et Zucc. (Styracaceae),[3] desacyl-boninsaponin A from the bark of *Schima mertensiana* Koidz. (Theaceae),[4] and sakuraso-saponin from the root of *Primula sieboldi* E. Morren (Primulaceae).[5] In these studies, branching points at C-2 and C-4 of the glucuronide moieties in the oligosaccharide portions were assumed, based on the identification of methyl 3-O-methylglucopyranoside (**i**), which was obtained by methanolysis of the lithium aluminum hydride ($LiAlH_4$) reduction products of the permethylated saponins. We have since utilized these glucuronide saponins as substrates for developing new selective cleavage methods for the glucuronide linkage in oligoglycosides.[6]

However, in the course of our recent study on the saponins from the seeds of *Aesculus turbinata* Blume (Hippocastanaceae),[7] we found that the previous identification methods (gas-liquid and thin-layer chromatography (GLC, TLC)[3–5] for methyl 3-O-methylglucopyranoside (**i**) was not precise enough to distinguish **i** from methyl 4-O-methylglucopyranoside (**ii**).[8] Therefore, the branching positions in the glucuronide moieties of the above-mentioned glucuronide saponins required reinvestigation.

The fully methylated derivatives (**1a**, **2a**, **3a**) of the three saponins were reduced with $LiAlH_4$ (giving **1b**, **2b**, **3b**) and then methylated by Kuhn's procedure[9] to afford the corre-

1) Part XXVII: I. Kitagawa, H. Yamanaka, M. Kobayashi, T. Nishino, I. Yosioka, and T. Sugawara, *Chem. Pharm. Bull.*, **26**, 3722 (1978).
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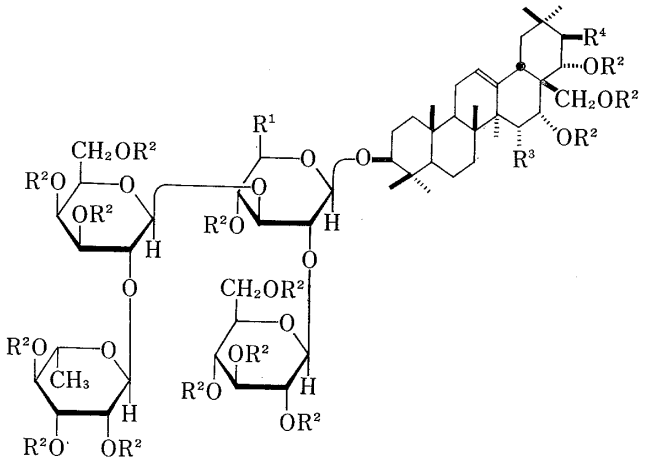
3) I. Kitagawa, Y. Imakura, T. Hayashi, and I. Yosioka, *Chem. Pharm. Bull.*, **23**, 1520 (1975).
4) I. Kitagawa, K.S. Im, and I. Yosioka, *Chem. Pharm. Bull.*, **24**, 1260 (1976).
5) I. Kitagawa, Y. Ikenishi, M. Yoshikawa, and I. Yosioka, *Chem. Pharm. Bull.*, **24**, 2470 (1976).
6) I. Kitagawa and M. Yoshikawa, *Heterocycles*, **8**, 783 (1977), and references cited therein.
7) I. Kitagawa, K. Kobayashi, and M. Yoshikawa, to be published.
8) It has been found recently that **i** and **ii** can be distinguished from each other by TLC using silica gel $60F_{254}$ (Merck) using double development with benzene–acetone (1: 1) (*Rf*: **i**=0.30; **ii**=0.24 (major), 0.27).
9) R. Kuhn, H. Trischmann, and I. Löw, *Angew. Chem.*, **67**, 32 (1955).

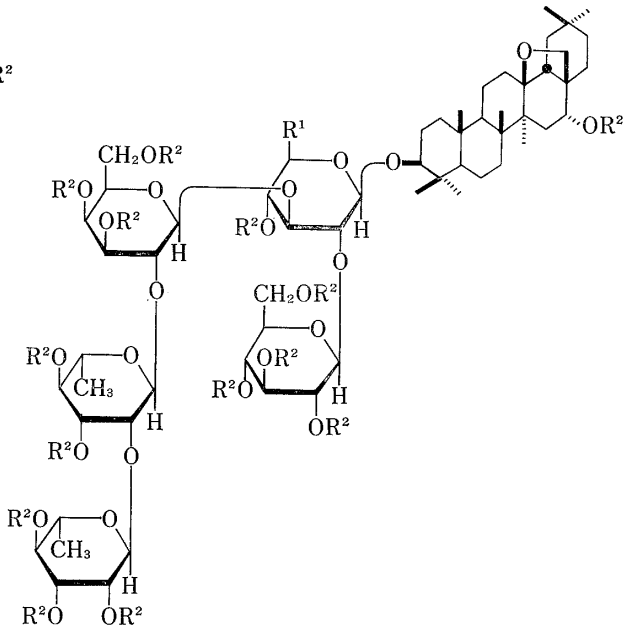
sponding glucosidic derivatives (**1c**, **2c**, **3c**). When these methylated products (**1c**, **2c**, **3c**) were subjected to methanolysis with hydrogen chloride in dry methanol, methyl 2,3,4-tri-O-methylrhamnopyranoside (**iii**), methyl 2,3,4,6-tetra-O-methylglucopyranoside (**iv**), methyl 3,4,6-tri-O-methylgalactopyranoside (**v**), and methyl 4,6-di-O-methylglucopyranoside (**vi**) were obtained as methylated monosaccharides from **1c** and **2c**, while **iii**, **iv**, **v**, methyl 3,4-di-O-methylrhamnopyranoside (**vii**), and **vi** (as from **1c** and **2c**) were obtained from **3c**.



1: R^1=COOH, R^2=R^3=H, R^4=OH (desacyl-jegosaponin)
1a: R^1=$COOCH_3$, R^2=CH_3, R^3=H, R^4=OCH_3
1b: R^1=CH_2OH, R^2=CH_3, R^3=H, R^4=OCH_3
1c: R^1=CH_2OCH_3, R^2=CH_3, R^3=H, R^4=OCH_3

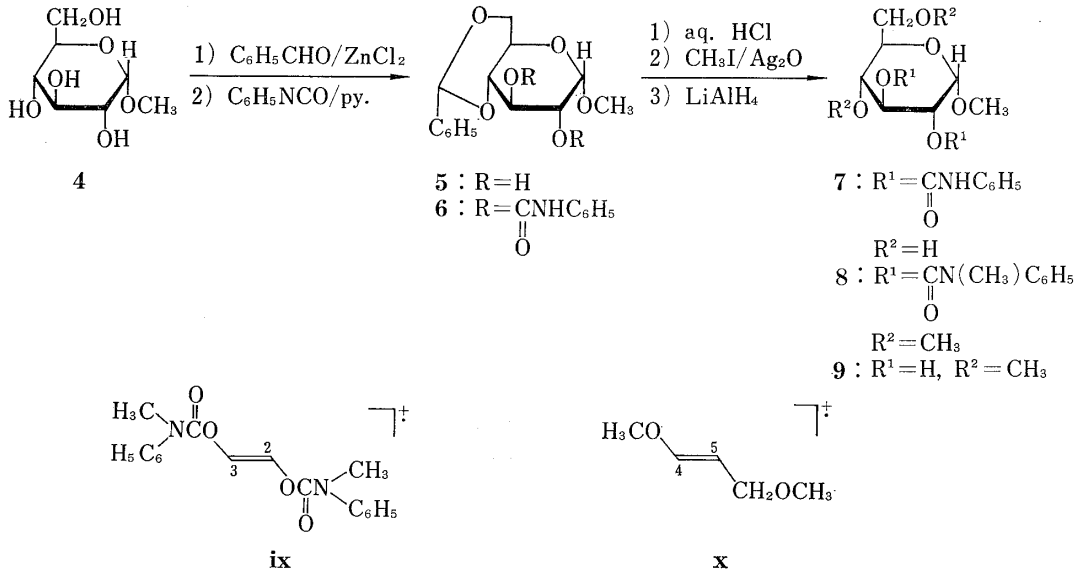
2: R^1=COOH, R^2=H, R^3=OH, R^4=H (desacyl-boninsaponin A)
2a: R^1=$COOCH_3$, R^2=CH_3, R^3=OCH_3, R^4=H
2b: R^1=CH_2OH, R^2=CH_3, R^3=OCH_3, R^4=H
2c: R^1=CH_2OCH_3, R^2=CH_3, R^3=OCH_3, R^4=H

Chart 1



3: R^1=COOH, R^2=H (sakuraso-saponin)
3a: R^1=$COOCH_3$, R^2=CH_3
3b: R^1=CH_2OH, R^2=CH_3
3c: R^1=CH_2OCH_3, R^2=CH_3

Chart 2



4

5: R=H
6: R=CNHC$_6$H$_5$ (O)

7: R^1=CNHC$_6$H$_5$ (O), R^2=H
8: R^1=CN(CH$_3$)C$_6$H$_5$ (O), R^2=CH_3
9: R^1=H, R^2=CH_3

ix

x

Chart 3

Since methyl 4,6-di-O-methylglucopyranoside (**vi**) rather than methyl 3,6-di-O-methylglucopyranoside (**viii**) has been identified as the methylated monosaccharide deriving from the glucuronide moiety in the parent saponins, the branching positions in the glucuronide moieties of these saponins must be at C-2 and C-3 rather than the previously assumed C-2 and C-4. Taking into consideration our previous work[3-5] together with the present results, it is evident that the branching positions in the glucuronide moieties of desacyl-jegosaponin, desacyl-boninsaponin A, and sakuraso-saponin should be revised to those shown in the structures **1**, **2**, and **3**, respectively (previous branching positions were erroneously given as C-2 and C-4).

An authentic sample of methyl 4,6-di-O-methylglucopyranoside (**vi**) was synthesized as shown in Chart 3. Methyl 4,6-O-benzylidene-α-D-glucopyranoside (**5**)[10] prepared from methyl α-D-glucopyranoside (**4**) was converted to the phenylurethane (**6**) by treatment with phenylisocyanate in pyridine. Removal of the protecting benzylidene group in **6** followed by methylation[9] gave **8**. The infrared (IR) spectrum of **8** shows no absorption band due to NH, while the proton magnetic resonance (^{1}H–NMR) spectrum shows signals due to three O-methyls and two N-methyls. These ^{1}H–NMR data, together with the mass spectral fragmentation pattern of **8**,[11] support the proposed structure. Finally, $LiAlH_4$ reduction of **8** yielded methyl 4,6-di-O-methyl-α-D-glucopyranoside (**9**),[12] which was then subjected to methanolysis and found to be identical by GLC and TLC with **vi** liberated from **1c**, **2c**, and **3c** as mentioned above.

In our previous reports on selective cleavage methods for the glucuronide linkage in oligoglycosides,[6] the reaction pathways were discussed on the basis of previously proposed structures of desacyl-jegosaponin and sakuraso-saponin. We are currently reinvestigating these results on the basis of the revised branching structures, and the results will be reported in due course.[13]

Experimental[14]

Hexadeca-O-methyl Derivative (1c) from Desacyl-jegosaponin (1)——As reported previously,[3] desacyl-jegosaponin (**1**, 1 g) was methylated by Hakomori's method[16] to give **1a** (650 mg), which was then reduced with $LiAlH_4$ in dry ether to furnish **1b** (600 mg). A solution of **1b** (500 mg) in dimethylformamide (DMF) (8 ml) was treated with CH_3I (15 ml) and Ag_2O (4.2 g) and stirred at 32° for 24 hr. After removing the inorganic material by filtration, the solution was diluted with ether and washed with water. The organic layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure. Preparative TLC (benzene–acetone=3:1) furnished **1c** (340 mg) and **1b** (130 mg, recovered). **1c**, white powder, $[\alpha]_D^{24}$ −25.7° (c=1.0, CCl_4). *Anal.* Calcd for $C_{70}H_{122}O_{24}$: C, 62.38; H, 9.13. Found: C, 62.20; H, 9.12. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2925, 1103, 1084. ^{1}H-NMR ($CDCl_3$, δ): 0.88—0.92 (15H), 1.04, 1.31 (3H each, both s) (*tert.* $CH_3\times7$), 1.25 (3H, d, J=5.5 Hz, *sec.* CH_3), 3.28, 3.32, 3.37, 3.40 (3H each, all s), 3.49—3.53 (36H) ($OCH_3\times16$), 4.27, 4.59, 4.98 (1H each, all d, J=7 Hz), 5.17 (1H, s) (anomeric H×4), 5.26 (1H, br. s, $W_{h/2}$=8 Hz) (olefinic H).

Hexadeca-O-methyl Derivative (2c) from Desacyl-boninsaponin A (2)——Desacyl-boninsaponin A (**2**, 500 mg) was methylated[16] to give **2a** (280 mg), which was then reduced with $LiAlH_4$ in dry ether to afford **2b** (240 mg) as reported previously.[4] A solution of **2b** (200 mg) in DMF (5 ml) was treated with CH_3I (10 ml) and Ag_2O (2 g) at 32° with stirring for 24 hr. After work-up as described for **1c**, the product was purified by preparative TLC (benzene–acetone=3:1) to furnish **2c** (140 mg) and **2b** (20 mg recovered). **2c**, white powder, $[\alpha]_D^{25}$ −22.6° (c=1.0, CCl_4). *Anal.* Calcd for $C_{70}H_{122}O_{24}$: C, 62.38; H, 9.13. Found: C, 62.56; H, 9.02. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2930, 1102. ^{1}H-NMR (CCl_4, δ): 0.83 (3H, s), 0.90—1.00 (15H), 1.25 (3H, s) (*tert.*

10) N.K. Richtmyer, "Methods in Carbohydrate Chemistry," Vol. I, ed. by R.L. Whistler and M.L. Wolfrom, Academic Press, New York and London, 1962, p. 108.
11) J. Lönngren and S. Svensson, *Advan. Carbohyd. Chem. and Biochem.*, **29**, 41 (1974).
12) D.J. Bell and J. Lorber, *J. Chem. Soc.*, **1940**, 453.
13) *cf.* I. Kitagawa, M. Yoshikawa, K. Shirakawa, T. Kamigauchi, M. Saito, and K. Kobayashi, The 2nd Symposium on Carbohydrates (Kyoto 1979, July), Symposium Paper, p. 16.
14) The instruments used to obtain the physical data, and the experimental conditions for chromatography were same as in our previous paper[15] unless otherwise specified.
15) I. Kitagawa A. Kadota, and M. Yoshikawa, *Chem. Pharm. Bull.*, **26**, 3825 (1978).
16) S. Hakomori, *J. Biochem.* (Tokyo), **55**, 205 (1964).

$CH_3 \times 7$), 1.28 (3H, d, $J=6$ Hz) (*sec.* CH_3), 3.25 (3H, s), 3.32, 3.34, 3.36, 3.39, 3.40 (6H each, all s), 3.47—3.52 (15H) ($OCH_3 \times 16$), 4.13 (1H, d, $J=7$ Hz), 4.50 (1H, d, $J=8$ Hz), 4.87 (1H, d, $J=7$ Hz), 4.91 (1H, s) (anomeric H×4), 5.28 (1H, br. s, $W_{h/2}=9$ Hz) (olefinic H).

Pentadeca-O-methyl Derivative (3c) from Sakuraso-saponin (3)——Sakuraso-saponin (**3**, 1 g) was methylated[16] and the product (**3a**, 700 mg) was reduced with $LiAlH_4$ in dry ether to give **3b** (640 mg) as reported previously.[5] **3b** (500 mg) in DMF (8 ml) was methylated with CH_3I (15 ml) and Ag_2O (4.2 g) as described for **1c**, and the product was purified by preparative TLC (benzene–acetone=3: 1) to furnish **3c** (320 mg) and **3b** (160 mg, recovered). **3c**, white powder, $[\alpha]_D^{24}$ −55.7° ($c=1.2$, CCl_4). *Anal.* Calcd for $C_{75}H_{130}O_{26}$: C, 62.22; H, 9.05. Found: C, 61.86; H, 9.05. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2930, 1100. ^{1}H-NMR ($CDCl_3$, δ): 0.87 (9H, s), 0.93, 1.01, 1.09, 1.15 (3H each, all s) (*tert.* $CH_3 \times 7$), 1.24, 1.27 (3H each, both d, $J=5.5$ Hz) (*sec.* $CH_3 \times 2$), 3.23, 3.30 (3H each, both s), 3.38 (6H, s), 3.49—3.59 (33H) ($OCH_3 \times 15$), 4.24, 4.54, 4.96 (1H each, all d, $J=$ 7 Hz), 5.02, 5.07 (1H each, both s) (anomeric H×5).

Methanolysis of 1c, 2c, and 3c——A solution of **1c**, **2c**, or **3c** (10 mg) in 9% HCl–dry MeOH (2 ml) was heated under reflux for 2 hr. The reaction mixture was neutralized with Ag_2CO_3 powder and filtered to remove inorganic material. The filtrate was concentrated under reduced pressure and the residue was analyzed by GLC and TLC.

From **1c** and **2c**, methyl 2,3,4-tri-O-methylrhamnopyranoside (**iii**), methyl 2,3,4,6-tetra-O-methylglucopyranoside (**iv**), methyl 3,4,6-tri-O-methylgalactopyranoside (**v**), and methyl 4,6-di-O-methylglucopyranoside (**vi**) (=**9**, *vide infra*) were identified. TLC (*Rf*)[17]: a) benzene–MeOH=15: 1, **iii** (0.44, 0.65); b) benzene–acetone=4: 1, **iii** (0.62, 0.75), **iv** (0.31, 0.42); c) benzene–acetone=1: 1 (developing twice), **v** (0.65, 0.68), **vi** (0.38, 0.42); d) $CHCl_3$–MeOH=10: 1 (developing twice), **v** (0.62, 0.70), **vi** (0.33, 0.39); e) AcOEt (developing twice), **v** (0.46), **vi** (0.31, 0.39). GLC (t_R): a) 15% polyneopentyl glycol succinate (NPGS) on Chromosorb WAW (80—100 mesh), 2 m×3 mm, column temp. 150°, carrier gas N_2, flow rate 30 ml/min, **iii** (3′25″ (major), 4′50″), **iv** (6′58″, 9′37″ (major)), **v** (24′50″ (major), 38′30″); b) 15% NPGS on Chromosorb WAW (80—100 mesh), 2 m×3 mm, column temp. 210°, N_2 flow rate 40 ml/min, **iv** (1′20″, 1′37″ (major)), **v** (3′06″ (major), 4′17″), **vi** (5′25″ (major), 6′24″); c) 15% diethylene glycol succinate (DEGS) on Chromosorb WAW (80—100 mesh), 1 m×3 mm, column temp. 210°, N_2 flow rate 30 ml/min, **iv** (53″, 1′07″ (major)), **v** (2′50″ (major), 4′18″), **vi** (6′00″ (major), 7′38″).

From **3c**, **iii**, **iv**, **v**, **vi**, and methyl 3,4-di-O-methylrhamnopyranoside (**vii**) were identified as methylated monosaccharides. TLC (*Rf*): f) benzene–acetone=2: 1, **iii** (0.56, 0.85), **iv** (0.39, 0.60), **v** (0.13, 0.21), **vi** (0.11, 0.12), **vii** (0.33, 0.42). GLC (t_R): d) 15% NPGS on Chromosorb WAW (80—100 mesh), 2 m×3 mm, column temp. 100°, N_2 flow rate 35 ml/min, **iii** (2′58″ (major), 4′10″), **iv** (5′55″, 8′05″ (major)), **v** (20′10″ (major), 30′30″), **vii** (5′32″ (major), 9′25″). Furthermore, **iii**, **iv**, **v**, and **vi** were identified from **3c** as in the case of **1c** and **2c** [TLC: a), b), c), d) and GLC: a), b), c)].

Phenylurethane (6) from D-Glucose——A solution of D-glucose (16.2 g) in 3% HCl–dry MeOH (65 ml) was heated under reflux for 3 hr. The reaction mixture was left to stand at 4° and the resulting colorless needles (**4**, 7.4 g, 42%) were collected by filtration. Recrystallization from methanol gave a pure sample of **4**, mp 164° (colorless needles), $[\alpha]_D^{24}$ +139.0° ($c=2.8$, H_2O) [lit.:[18] mp 165° (MeOH), $[\alpha]_D^{25}$ +157° (H_2O)].

A solution of **4** (15 g) in benzaldehyde (38 ml) was treated with $ZnCl_2$ (11.3 g) and stirred at room temperature (12°) for 6 hr. Cold water (330 ml) was added and the mixture was left to stand at 5° for 12 hr, treated with petr. ether (25 ml), and stirred for 30 min. The resulting white precipitates were collected by filtration to give **5** (20.1 g, 92%). Recrystallization from $CHCl_3$–ether furnished **5** as colorless needles of mp 163—164°, $[\alpha]_D^{24}$ +119.0° ($c=1.1$, $CHCl_3$), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3574, 3462, 3005, 2941, 1467. ^{1}H-NMR ($CDCl_3$, δ): 3.39 (3H, s, OCH_3), 4.67 (1H, d, $J=4.5$ Hz, anomeric H), 5.46 (1H, s, benzal H), 7.21—7.51 (5H, m, phenyl H×5) [lit.[10]: mp 163—164° ($CHCl_3$–ether), $[\alpha]_D^{20}$ +110° ($CHCl_3$)].

A solution of **5** (14 g) in pyridine (100 ml) was treated with phenylisocyanate (26 ml) and the total mixture was heated under reflux for 2 hr. After cooling, the reaction mixture was diluted with MeOH (50 ml) and heated again under reflux for 10 min. The reaction mixture was then poured into ice-water and extracted with $CHCl_3$. The $CHCl_3$ extract was then taken and dried over $MgSO_4$. The product (60 g) obtained by removal of the solvent under reduced pressure was purified by column chromatography (silica gel, Merck, 70—230 mesh, 2 kg, benzene–acetone=80: 1→40: 1) to furnish **6** (22 g, 85%). **6**, mp 214—217° (colorless needles from MeOH), $[\alpha]_D^{24}$ +32.5° ($c=0.9$, $CHCl_3$). *Anal.* Calcd for $C_{28}H_{28}O_8N_2$: C, 64.61; H, 5.42; N, 5.38. Found: C, 64.70; H, 5.32; N, 5.40. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3438, 1754, 1606, 1538, 1450, 1315. ^{1}H-NMR (d_6-acetone, δ): 3.46 (3H, s, OCH_3), 4.87 (1H, d.d, $J=4.5$, 10 Hz, 2-H), 5.06 (1H, d, $J=$ 4.5 Hz, 1-H), 5.49 (1H, d.d, $J=10$, 10 Hz, 3-H), 5.64 (1H, s, benzal H), 6.92 —7.58 (15H, m, phenyl H× 15), 8.68, 8.98 (1H each, both s, $W_{h/2}=4.5$, 5.5 Hz, exchangeable with D_2O, NH×2) [lit.[19]: mp 216—217° (MeOH), $[\alpha]_D^{25}$ +40° ($CHCl_3$)].

17) The *Rf* values for methylated monosaccharides which ran close to the top and bottom are omitted.
18) B. Helferich and W. Schäfer, "Organic Syntheses," Coll. Vol. I, ed. by H. Gilman, John Wiley and Sons, Inc., New York, London, 1941, p. 364.
19) W.M. Hearon, G.D. Hiatt, and C.R. Fordyce, *J. Am. Chem. Soc.*, **66**, 995 (1944).

Methyl 4,6-Di-O-methyl-α-D-glucopyranoside (9)——A solution of **6** (2.2 g) in acetone (30 ml) was treated with 0.8% aq. HCl (8 ml) and heated under reflux for 2 hr. After neutralization with Amberlite IRA-400 (OH^- form, 10 ml), the reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to yield a residue, which was crystallized from $CHCl_3$–*n*-hexane to furnish **7** (1.72 g, 98%) as colorless needles of mp 159—161°, $[\alpha]_D^{25}$ +55.8° (c=0.8, pyridine). *Anal.* Calcd for $C_{21}H_{24}O_8N_2$: C, 58.33; H, 5.59; N, 6.48. Found: C, 58.33; H, 5.47; N, 6.53. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3432, 1740, 1603, 1531, 1447. ^{1}H-NMR (d_6-acetone, δ): 3.39 (3H, s, OCH_3), 4.74 (1H, d.d, J=3.5, 11 Hz, 2-H), 4.96 (1H, d, J=3.5 Hz, 1-H), 5.25 (1H, m, 3-H), 6.84—7.53 (10H, m, phenyl H×10), 8.67, 8.92 (1H each, both br.s, $W_{h/2}$=3.5 Hz, NH×2) [lit.[19]: mp 151—153° (ligroin-AcOEt), $[\alpha]_D^{25}$ +55° (pyridine)].

A solution of **7** (600 mg) in DMF (8 ml) was treated with CH_3I (14.4 ml) and Ag_2O (5.4 g) and stirred at 31° for 24 hr in the dark. After removing inorganic material by filtration, the filtrate was concentrated under reduced pressure. The product (660 mg) was purified by column chromatography (silica gel, 50 g, benzene–AcOE =30: 1→10: 1) to furnish **8** (636 mg, 92%). **8**, colorless oil, $[\alpha]_D^{24}$ +128.2° (c=0.8, $CHCl_3$). High resolution mass spectrum: Calcd for $C_{25}H_{32}O_8N_2$ (M^+): 488.216, $C_{18}H_{18}O_4N_2$ (**ix**): 326.125, $C_5H_{10}O_2$ (**x**): 102.068. Found: 488.214, 326.123, 102.068. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1596, 1497, 1155, 1062. ^{1}H-NMR ($CDCl_3$, δ): 3.28, 3.32, 3.37 (3H each, all s), 3.35 (6H, s) (OCH_3×3, NCH_3×2), 4.65 (1H, d.d, J=4, 9 Hz, 2-H), 4.97 (1H, d, J=4, 1-H), 5.33 (1H, d.d, J=9, 9 Hz, 3-H), 7.05—7.34 (10H, m, phenyl H×10).

A suspension of $LiAlH_4$ (60 mg) in dry ether (5 ml) was added dropwise to a solution of **8** (270 mg) in dry ether (10 ml), and the whole was heated under reflux for 1 hr. After cooling, the reaction was terminated by adding aq. ether and the mixture was neutralized with Dowex 50w×8 (H^+ form, 5 ml). After removing the resin by filtration, the filtrate was concentrated under reduced pressure. The residue was then purified by preparative TLC (benzene–acetone=3: 5) to furnish methyl 4,6-di-O-methyl-α-D-glucopyranoside (**9**, 106 mg, 86%). **9**, colorless oil, $[\alpha]_D^{24}$ +159.0° (c=1.1, $CHCl_3$). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3404, 2918, 1069. ^{1}H-NMR ($CDCl_3$, δ): 3.43 (6H, s), 3.56 (3H, s) (OCH_3×3), 4.74 (1H, d, J=2 Hz, 1-H) [lit.:[12] $[\alpha]_D$ +157° ($CHCl_3$)]. A solution of **9** in 9% HCl–dry MeOH (1.5 ml) was heated under reflux for 2 hr, then neutralized with Ag_2CO_3. The product obtained by concentration of the filtrate was used for identification of **vi** by GLC and TLC as described above.