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Chemical Transformation of Uronic Acids Leading to Aminocyclitols. V.[1] Syntheses of Aminocyclitol-oligosides from Glucuronide-saponins by Means of Lead Tetraacetate Oxidation

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By means of a decarboxylative acetoxylation induced by lead tetraacetate and a subsequent nitromethane cyclization reaction, methylated derivatives (**1a**, **4a**, **7a**) of three glucuronide-saponins [sakuraso-saponin (**1**), desacyl-jegosaponin (**4**), and soyasaponin I (**7**)] were decomposed selectively at the glucuronide linkage to furnish the methylated genuine aglycones (**2**, **5**, **8**) and *scyllo*-nitrocyclitol-oligosides (**3**, **6**, **9**). The oligosides were further converted to *scyllo*-aminocyclitol-oligosides (**3a**, **6a**, **9a**), thus accomplishing syntheses of aminocyclitol-oligosides by making use of the oligosaccharide moieties in glucuronide-saponins.

Keywords——glucuronide-saponin; sakuraso-saponin; desacyl-jegosaponin; soyasaponin I; lead tetraacetate oxidative decarboxylation; nitromethane cyclization; nitrocyclitol-oligoside; aminocyclitol-oligoside

By employing an oxidative decarboxylation reaction as the key step, which was initiated either with lead tetraacetate or electrochemically, we have developed two versatile methods for the conversion of various carbohydrates to cyclitol derivatives.[1-3] In the case of lead tetraacetate-mediated cyclitol syntheses, the hydroxyl groups in the starting carbohydrates must be protected, but the overall yields were generally satisfactory. Through this procedure, we have so far been successful in the syntheses of cyclitols such as streptamine hexaacetate,[2b] 2-deoxystreptamine pentaacetate,[2c] (−)-shikimic acid, (−)-quinic acid,[2c] and an aminoglycoside antibiotic paromamine.[2d] On the other hand, electrochemically mediated cyclitol syntheses were shown to be useful for syntheses of aminocyclitols such as streptamine hexaacetate[1] and were especially convenient for the preparation of *myo*-aminocyclitol-oligosides from the oligosaccharide moieties of glucuronide-saponins.[3a,b]

As a continuation of this work, we have investigated the application of the lead tetraacetate-mediated cyclitol syntheses to glucuronide-saponins. This paper deals with syntheses of *scyllo*-aminocyclitol-oligosides from the oligosaccharide moieties of glucuronide-saponins.

Aminocyclitol-tetraglycoside (3a) from Sakuraso-saponin (1)

As a selective cleavage method for the glucuronide linkage in oligosides, we have developed a lead tetraacetate-mediated method involving the reaction pathway shown in Chart 1.[4] If the presumed dialdehyde intermediate (**iv**) could be trapped with alkaline nitromethane, aminocyclitol-oligosides might be synthesized from glucuronide-saponins, as found in the previous electrochemical conversions.[3b]

Sakuraso-saponin (**1**), from the root of *Primula sieboldi* E. MORREN,[5] was converted to a methylated carboxyl-free derivative (**1a**),[5,6] which was subjected to lead tetraacetate oxidation. Treatment of the acetoxylated product (**1b**)[5,6] with nitromethane in the presence of

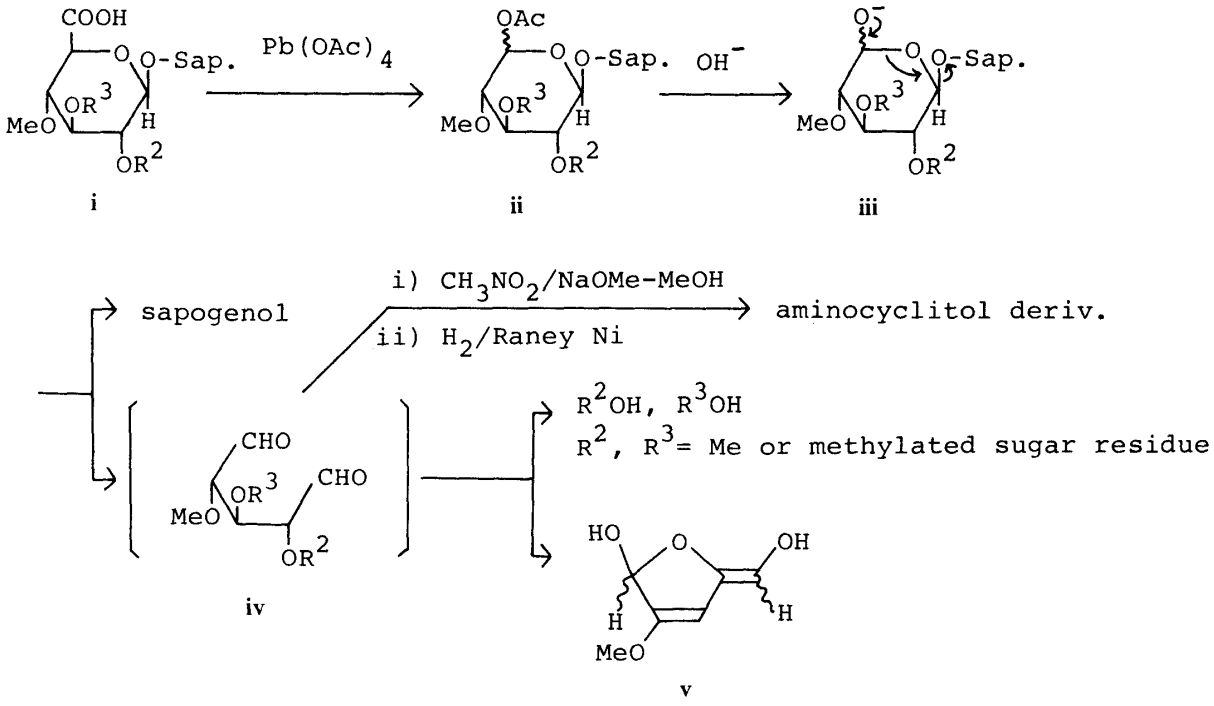

Chart 1

methanolic sodium methoxide yielded 16-*O*-methylprotoprimulagenin A (**2**, 87%) and a nitrocyclitol-oligoside (**3**, 44%) as the major oligoside. The structure of **2** was supported by the physical data and by conversion of **2** to the 3-*O*-acetate (**2a**).[6] The structure of **3** was proved by the following evidence.

The infrared (IR) spectrum of **3** showed absorption bands due to hydroxyl and nitro groups, whereas the proton nuclear magnetic resonance (^{1}H-NMR) spectrum (in d_6-acetone) of **3** showed signals assignable to four anomeric protons in one galactoside, one glucoside, and two rhamnoside moieties, together with signals due to two secondary methyl groups in two rhamnoside residues and thirteen methoxyl groups. Thus, retention of the oligosaccharide branch of **1** in **3** has been supported.

Catalytic reduction of **3** over Raney Ni (T-4)[7] and subsequent acetylation furnished an aminocyclitol-oligoside (**3a**, 71%). The molecular ion peak (*m/z* 1103) of **3a** was observed in the field desorption mass spectrum (FD-MS). The IR spectrum of **3a** showed absorption bands due to amide and acetoxyl functions. The ^{1}H-NMR spectrum [in d_6-dimethyl sulfoxide (DMSO)] showed signals assignable to two secondary methyl groups, thirteen methoxyl groups, one acetylamino group, and two acetoxyl groups. In addition, the ^{1}H-NMR spectrum showed signals assignable to cyclitol protons attached to C-2 and C-6, each bearing an acetoxyl function. The signals due to the acetylamino group and acetoxyl groups were also observed at δ 1.94 (3H) and δ 2.03 (6H), respectively, in the ^{1}H-NMR spectrum taken in $CDCl_3$. From these chemical shifts, one acetylamino and two acetoxyl groups in **3a** were assigned as equatorial.[8] Therefore, the cyclitol moiety in **3a** has been shown to be *scyllo*.

Methanolysis of **3a** provided methyl 2,3,4-tri-*O*-methylrhamnopyranoside (**a**), methyl 3,4-di-*O*-methylrhamnopyranoside (**b**), methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**c**), and methyl 3,4,6-tri-*O*-methylgalactopyranoside (**d**).[9] Thus the structure of **3a**, which retains the oligosaccharide branch of **1**, was confirmed.

Aminocyclitol-triglycoside (6a) from Desacyl-jegosaponin (4)

A methylated carboxyl-free derivative (**4a**),[5,6] which was prepared from desacyl-

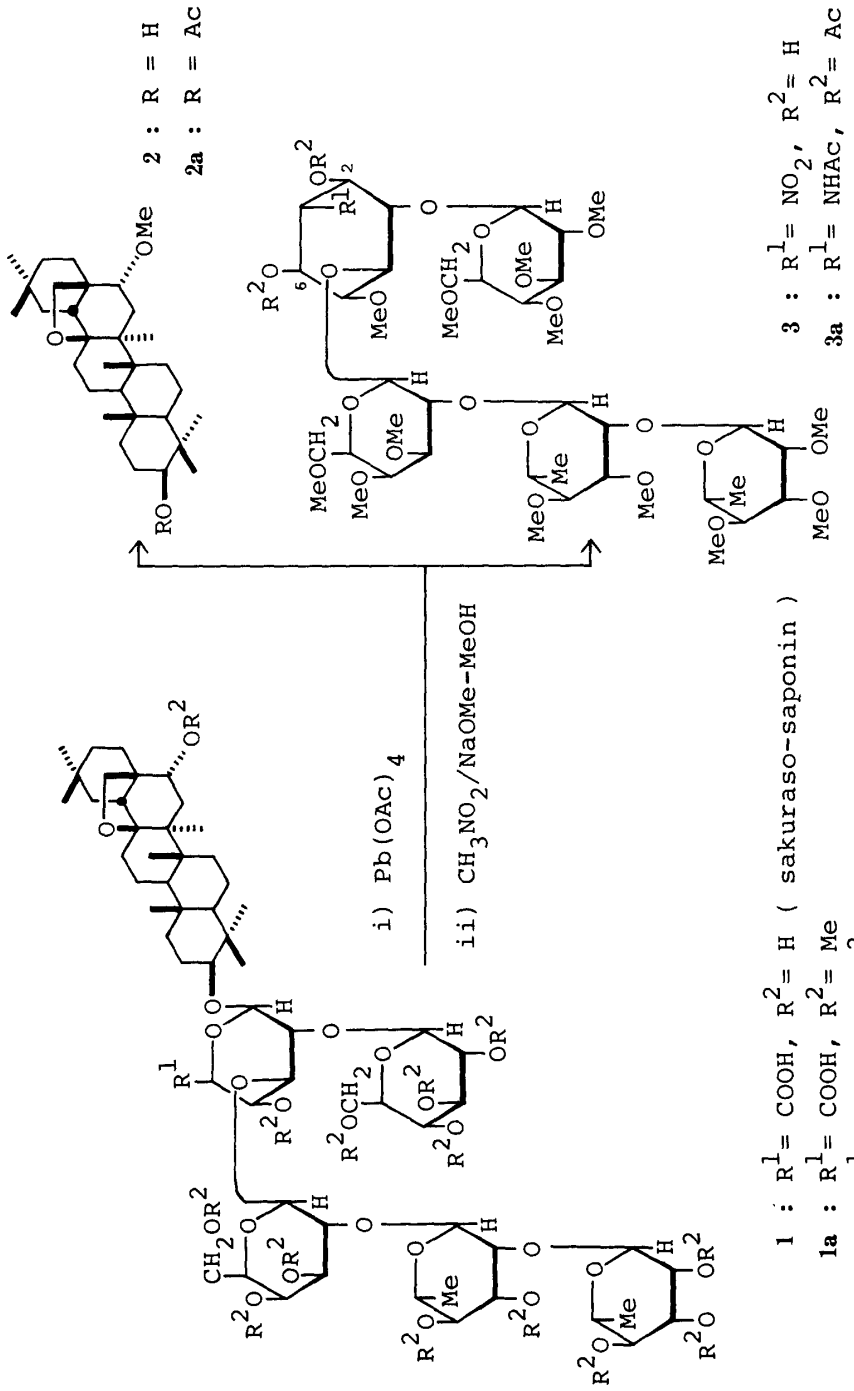

Chart 2

jegosaponin (**4**) (obtained from the pericarps of *Styrax japonica* SIEB. *et* ZUCC.[5]), was subjected to decarboxylative acetoxylation and subsequent nitromethane cyclization as carried out for **1** to yield 16,21,22,28-tetra-*O*-methylbarringtogenol C (**5**, 65%) and a nitrocyclitol-oligoside (**6**, 38%) as the major oligoside.

The structure of **5** was confirmed by conversion of **5** to the 3-*O*-acetate (**5a**).[6] The IR spectrum of **6** showed absorption bands due to hydroxyl and nitro groups. The ^{1}H-NMR spectrum (d_6-acetone) showed signals assignable to one secondary methyl group in the rhamnoside moiety, eleven methoxyl groups, and three anomeric protons on the galactoside, glucoside, and rhamnoside moieties. Thus, the carbohydrate branch of **4** in **6** is retained.

Catalytic reduction followed by acetylation of **6** as carried out for **3** yielded an acetylaminocyclitol-oligoside (**6a**) in high yield. The molecular composition of **6a** was obtained from the FD-MS. The IR spectrum of **6a** suggested the presence of amide and acetoxyl groups, whereas the ^{1}H-NMR spectrum (d_6-DMSO) indicated that these groups were all equatorial (from their chemical shifts).[8] The ^{1}H-NMR spectrum also showed a two-proton triplet ($J=11$ Hz) assignable to 2-H and 6-H in the cyclitol moiety which were geminal to an equatorial acetoxyl group. Thus, the *scyllo* configuration of the cyclitol moiety in **6a** was deduced. Furthermore, methanolysis of **6a** liberating methyl glycosides (**a**, **c**, **d**)[9] corroborated the carbohydrate sequence in **4**.

Aminocyclitol-diglycoside (9a) from Soyasaponin I (7)

Soyasaponin I (**7**) from soybean (*Glycine max* MERRILL, seeds)[10] was converted to a carboxyl-free methylated derivative (**7a**) in a manner similar to that mentioned above. Lead tetraacetate-mediated decarboxylation of **7a** followed by nitromethane cyclization provided 22,24-di-*O*-methylsoyasapogenol B (**8**)[10] in high yield and a nitrocyclitol-diglycoside (**9**)[11] in low yield. Thin-layer chromatography (TLC) of the oligoside fraction showed the formation of some related isomers of **9** although they could not be isolated.

The IR and ^{1}H-NMR spectra of **9** supported the structure, as described above for **3** and **6**. Further, a triplet ($J=10$ Hz) due to a proton at C-1 bearing a nitro group in the cyclitol moiety indicated the *scyllo*-cyclitol configuration. An acetylaminocyclitol-diglycoside (**9a**) was prepared from **9** through the same procedure as used for **3** and **6**. Here again, the molecular ion peak of **9a** was obtained in the FD-MS. The presence of one equatorial acetamide group and two equatorial acetoxyl groups was suggested by the IR and ^{1}H-NMR (d_6-DMSO) spectra. The ^{1}H-NMR spectrum taken in $CDCl_3$ showed a two-proton broad triplet ($J=ca.$ 10 Hz) assignable to 2-H and 6-H in the cyclitol moiety. Furthermore, methanolysis of **9a** liberated two methyl glycosides (**a**, **d**), thus substantiating the structure of **9a**.

Through the lead tetraacetate-mediated conversion, three *scyllo*-aminocyclitol-oligosides (**3a**, **6a**, **9a**) were obtained as major oligosides from sakuraso-saponin (**1**), desacyl-jegosaponin (**4**), and soyasaponin I (**7**), respectively, *via* their methylated derivatives (**1a**, **4a**, **7a**). On the other hand, in our previous electrochemically mediated conversions, **1** and **4** were transformed to the corresponding *myo*-aminocyclitol-oligosides.[3b] In the electrochemical procedures, the hydroxyl groups in the starting glucuronide-saponins were unprotected. Since the intermediary nitrocyclitol-oligosides were rather labile in alkaline medium, the alkaline nitromethane cyclizations should be carried out for a short period, resulting in the formation of the kinetically favored[11] *myo*-nitrocyclitol-oligosides.

However, the hydroxyl-protected nitrocyclitol-oligosides (**3**, **6**, **9**) were stable in alkaline medium and prolonged alkaline nitromethane treatments were possible, thus providing the thermodynamically favored[11] *scyllo*-nitrocyclitol derivatives as major oligosides. Therefore, the lead tetraacetate-mediated conversion method from carbohydrates to aminocyclitols seems to be useful for syntheses of *scyllo*-aminocyclitol derivatives, *i.e.* streptamine, 2-deoxystreptamine, *scyllo*-inosamine, and their glycosides, although deprotection procedures

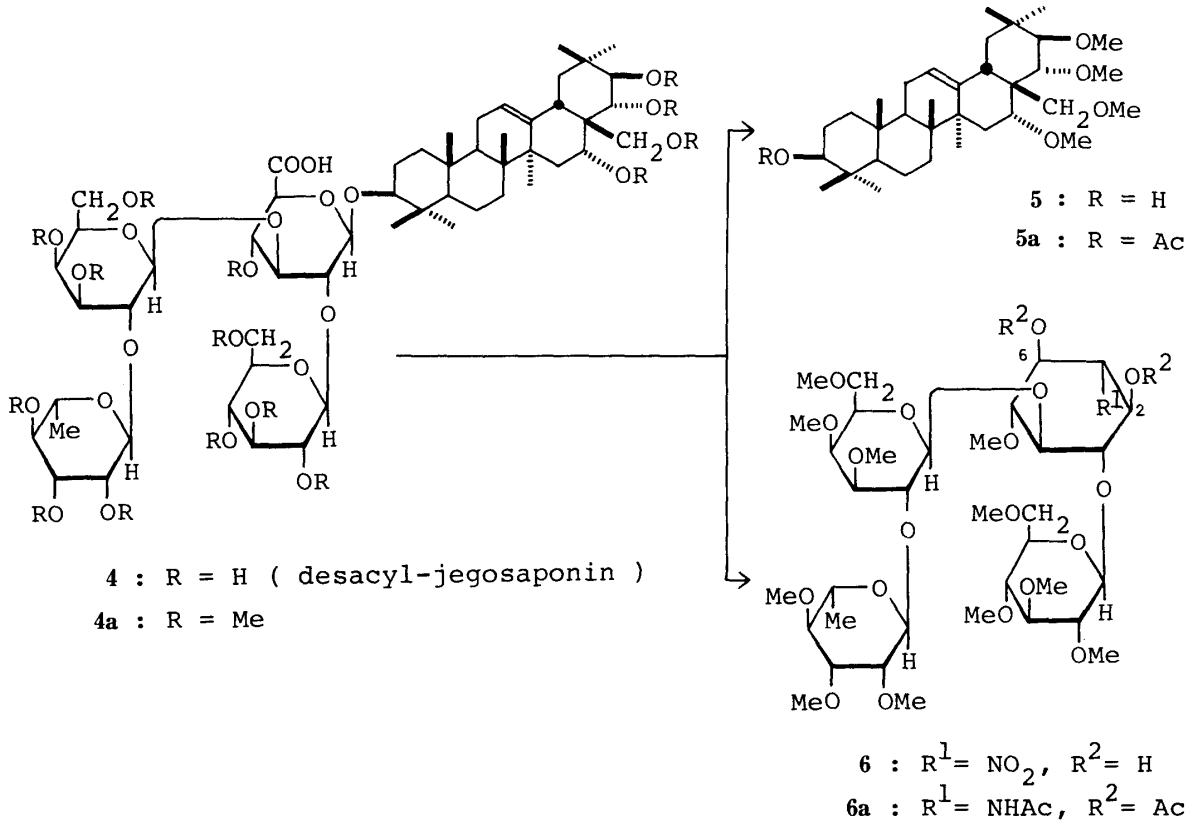

Chart 3-1

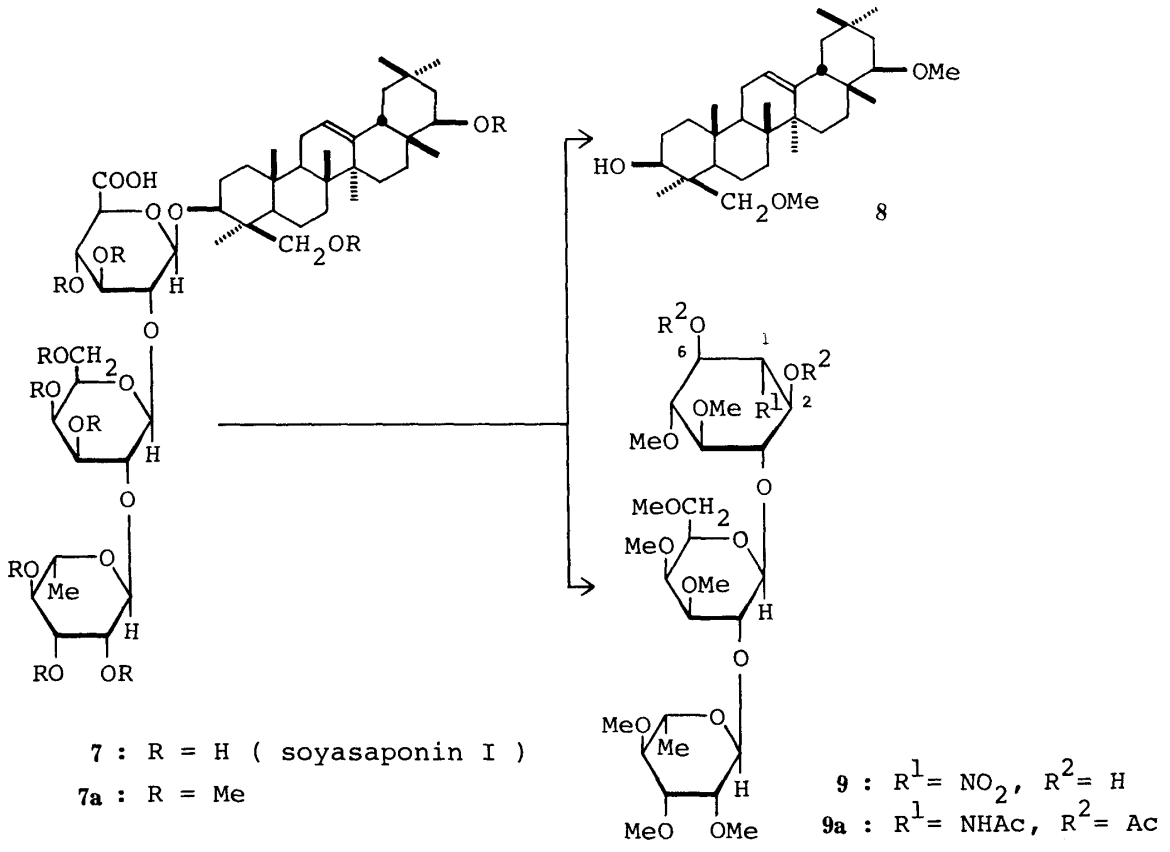

Chart 3-2

are required. Furthermore, the methylated aminocyclitol-oligosides (*e.g.* **3a**, **6a**, **9a**) may be useful for elucidation of the carbohydrate sequences in the parent glucuronide-saponins,[12] particularly in the structure elucidation of uronic acid-containing polysaccharides.

Experimental[13]

Nitromethane Treatment of 1b——Under an N_2 atmosphere, a solution of **1b** (463 mg)[5,6] in MeOH (3 ml) and CH_3NO_2 (10 ml) was treated with 5% NaOMe–MeOH (3 ml) and the whole solution was stirred at 30 °C for 3 d. The reaction mixture was neutralized with AcCl–MeOH (3 : 20) and made weakly acidic with AcOH, then the solvent was evaporated off under reduced pressure. The residue was treated with AcOEt and the insoluble portion was removed by filtration. Removal of the solvent from the filtrate under reduced pressure gave a product which was purified by column chromatography (SiO_2 40 g, benzene–acetone = 5 : 1) to furnish **2** (130 mg, 87%) and a mixture of nitrocyclitol-oligosides (220 mg). The latter was further purified by column chromatography (SiO_2 20 g, benzene–acetone = 3 : 1) and crystallized from benzene–acetone to give **3** (140 mg, 44%). **2**, white powder,[14] $[\alpha]_D^{19}$ +6.5° (*c* = 0.40, $CHCl_3$). High resolution MS (*m/z*): Calcd for $C_{31}H_{52}O_3$: 472.391. Found: 472.391. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620. ^{1}H-NMR ($CDCl_3$, δ): 0.75, 0.92, 0.96, 1.09, 1.15 (3H each, all s, *tert*-CH_3 × 5), 0.86 (6H, s, *tert*-CH_3 × 2), 3.21 (3H, s, OCH_3). **3**, mp 180—183 °C (colorless needles from benzene–acetone), $[\alpha]_D^{18}$ −49.2° (*c* = 1.04, $CHCl_3$). *Anal.* Calcd for $C_{43}H_{77}NO_{25}$: C, 51.23; H, 7.70; N, 1.39. Found: C, 51.47; H, 7.69; N, 1.48. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3425, 1560, 1383. ^{1}H-NMR (d_6-acetone, δ): 1.23, 1.30 (3H each, both d, *J* = 5 Hz, *sec*-CH_3 in rhamnose × 2), 3.32, 3.34 (3H each, both s, OCH_3 × 2), 3.43 (6H, s, OCH_3 × 2), 3.48, 3.50, 3.58 (9H each, all s, OCH_3 × 9), 4.41 (1H, d, *J* = 6.5 Hz), 4.55 (1H, d, *J* = 8 Hz) (anom. H in glucoside and galactoside), 5.00, 5.21 (1H each, both br s, $W_{h/2}$ = 5 Hz, anom. H in two rhamnosides).

Acetylation of 2——A solution of **2** (20 mg) in Ac_2O–pyridine (1 : 1, 1 ml) was allowed to stand at 35 °C for 12 h. The reaction mixture was poured into ice-water and the precipitates collected by filtration were crystallized from acetone to furnish **2a** (17 mg). **2a** was shown to be identical with an authentic sample[6] by mixed mp, TLC (benzene–acetone = 30 : 1; $CHCl_3$; *n*-hexane–AcOEt = 10 : 1), and IR (CCl_4) comparisons.

Reduction Followed by Acetylation of 3 Giving 3a——A suspension of Raney Ni (T-4) in EtOH (10 ml)[7] was added to a solution of **3** (120 mg) in EtOH (10 ml) and the mixture was shaken under a hydrogen atmosphere at 20 °C for 4 h. Removal of the solvent from the filtrate under reduced pressure yielded a product which was acetylated with Ac_2O (5 ml) and pyridine (7 ml) at 30 °C with stirring for 15 h. The reaction mixture was poured into ice-water and extracted with AcOEt. Work-up of the AcOEt extract in the usual manner gave a product, which was purified by column chromatography (SiO_2 10 g, benzene–acetone = 1 : 1) to furnish **3a** (92 mg, 71%). **3a**, white powder, $[\alpha]_D^{17}$ −32.6° (*c* = 2.40, MeOH). *Anal.* Calcd for $C_{49}H_{85}NO_{26}$: C, 53.30; H, 7.76; N, 1.27. Found: C, 53.85; H, 8.03; N, 1.30. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3360, 1740, 1684, 1538, 1240. ^{1}H-NMR ($CDCl_3$, δ): 1.27, 1.31 (3H each, both d, *J* = 6 Hz, *sec*-CH_3 in rhamnose × 2), 1.94 (3H, s, eq. NAc), 2.03 (6H, s, eq. OAc × 2), 3.41, 3.56, 3.60 (9H each, all s), 3.52 (12H, s) (OCH_3 × 13), 5.05, 5.42 (1H each, both br s, $W_{h/2}$ = 5 Hz, anom. H in two rhamnosides), 5.92 (1H, br s, $W_{h/2}$ = 10 Hz, exchangeable with D_2O, NH). ^{1}H-NMR (d_6-DMSO, δ): 1.17 (6H, d, *J* = 5 Hz, *sec*-CH_3 in rhamnose × 2), 1.75 (3H, s, eq. NAc), 1.93, 1.97 (3H each, both s, eq. OAc × 2), 3.27 (3H, s), 3.36, 3.42 (15H each, both s), 3.50 (6H, s) (OCH_3 × 13), 4.71 (2H, br t, *J* = 11 Hz, 2,6-H_2), 4.95, 5.15 (1H each, both br s, $W_{h/2}$ = 5 Hz, anom. H in two rhamnosides), 7.07 (1H, d, *J* = 8 Hz, exchangeable with D_2O, NH). FD-MS (*m/z*): 1103 (M^+, 100%).

Methanolysis of 3a——A solution of **3a** (5 mg) in AcCl–MeOH (3 : 20, 1 ml) was refluxed for 4 h. The reaction mixture was neutralized with Ag_2CO_3 and filtered. Removal of the solvent from the filtrate under reduced pressure yielded a mixture of methyl glycosides, from which 2,3,4-tri-*O*-methylrhamnopyranoside (**a**), methyl 3,4-di-*O*-methylrhamnopyranoside (**b**), methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**c**), and methyl 3,4,6-tri-*O*-methylgalactopyranoside (**d**) were identified by TLC and GLC comparisons. TLC: i) benzene–acetone = 2 : 1; ii) $CHCl_3$–MeOH = 20 : 1; iii) AcOEt; iv) benzene–MeOH = 15 : 1. GLC: i) 15% polyneopentylglycol succinate on Chromosorb WAW (80—100 mesh), 3 mm × 2 m, column temp. 150 °C, carrier gas N_2, flow rate 35 ml/min; t_R: **a** 2′58″ (major), 4′10″, **b** 5′32″ (major), 9′25″, **c** 5′55″, 8′05″ (major), **d** 20′10″ (major), 30′30″. ii) column temp. was 172 °C and the other conditions were the same as for i); t_R: **d** 3′15″ (major), 16′48″.[15]

Lead Tetraacetate Oxidation Followed by Nitromethane Treatment of 4a——A solution of **4a** (715 mg) in benzene (40 ml) was treated with $Pb(OAc)_4$ (1.3 g) and the mixture was heated under reflux for 3 h. After cooling, the reaction mixture was diluted with AcOEt and the whole mixture was washed with water, then dried over $MgSO_4$. Removal of the solvent from the filtrate under reduced pressure furnished a product (692 mg, 96%).[5,6] A solution of the product (647 mg) in MeOH (5 ml)–CH_3NO_2 (12 ml) was treated with 10% NaOMe–MeOH (2 ml) and the mixture was stirred at 35 °C for 2 d. Work-up of the reaction mixture as described above for **1b** gave a product, which was subjected to column chromatography (SiO_2 70 g, benzene–acetone = 40 : 1—4 : 1) to furnish **5** (222 mg, 85%) and a mixture of nitrocyclitol-oligosides (180 mg). Further purification of the oligoside mixture by column chromatography (SiO_2 15 g, benzene–acetone = 2 : 1) and crystallization of the product from ether afforded **6** (149 mg, 38%). **5**, white powder, $[\alpha]_D^{19}$ +18.0° (*c* = 0.20, $CHCl_3$). High resolution MS (*m/z*): Calcd for $C_{34}H_{58}O_5$: 546.428. Found: 546.428. IR $\nu_{max}^{CCl_4}$ cm^{-1}:

3625. ^{1}H-NMR (CCl_4, δ): 0.73, 0.82, 0.87, 0.88, 0.92, 0.94, 1.28 (3H each, all s, *tert*-$CH_3 \times 7$), 3.22, 3.24, 3.42, 3.46 (3H each, all s, $OCH_3 \times 4$), 5.22 (1H, br s, $W_{h/2} = 7$ Hz, 12-H). **6**, mp 136—139 °C (colorless needles from ether), $[\alpha]_D^{19}$ −37.0° ($c = 1.12$, $CHCl_3$). *Anal.* Calcd for $C_{35}H_{63}NO_{21}$: C, 50.41; H, 7.62; N, 1.68. Found: C, 50.17; H, 7.48; N, 1.66. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 1560, 1380. ^{1}H-NMR (d_6-acetone, δ): 1.24 (3H, d, $J = 6$ Hz, *sec*-CH_3 in rhamnose), 3.31, 3.34, 3.50 (3H each, all s), 3.42, 3.48, 3.52, 3.57 (6H each, all s) ($OCH_3 \times 11$), 4.41 (1H, d, $J = 7$ Hz), 4.55 (1H, d, $J = 8$ Hz) (anom. H in glucoside and galactoside), 5.21 (1H, br s, $W_{h/2} = 5$ Hz, anom. H in rhamnoside).

Acetylation of 5 Giving 5a——A solution of **5** (20 mg) in Ac_2O–pyridine (1 : 1, 1 ml) was allowed to stand at 35 °C for 12 h. The reaction mixture was poured into ice-water to afford **5a** (15 mg). **5a** thus obtained was shown to be identical with an authentic sample[9] by TLC (benzene–acetone = 30 : 1) and IR (CCl_4) comparisons.

Reduction Followed by Acetylation of 6 Giving 6a——A solution of **6** (110 mg) in EtOH (10 ml) was treated with a suspension of Raney Ni (T-4) in EtOH (15 ml) and the mixture was shaken under a hydrogen atmosphere at 25 °C for 2 h. Work-up of the reaction mixture as described above for **3** gave a product, which was acetylated with Ac_2O–pyridine (1 : 1, 1 ml) at 35 °C with stirring for 15 h. Usual work-up of the reaction mixture followed by column chromatography (SiO_2 10 g, benzene–acetone = 1 : 1) furnished **6a** (100 mg, 81%). **6a**, white powder, $[\alpha]_D^{17}$ −32.5° (c = 1.67, MeOH). *Anal.* Calcd for $C_{41}H_{71}NO_{22}$: C, 52.95, H, 7.70; N, 1.51. Found: C, 52.74; H, 7.93; N, 1.48. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3350, 1740, 1678, 1532, 1235. ^{1}H-NMR ($CDCl_3$, δ): 1.33 (3H, d, $J = 6$ Hz, *sec*-CH_3 in rhamnose), 1.95 (3H, s, eq. NAc), 2.06 (6H, s, eq. OAc × 2), 3.34, 3.49, 3.53, 3.56, 3.59 (3H each, all s), 3.43, 3.46, 3.63 (6H each, all s) ($OCH_3 \times 11$), 5.55 (1H, br s, $W_{h/2} = 5$ Hz, anom. H in rhamnoside), 5.91 (1H, d, $J = 8$ Hz, exchangeable with D_2O, NH). ^{1}H-NMR (d_6-DMSO, δ): 1.11 (3H, d, $J = 6$ Hz, *sec*-CH_3 in rhamnose), 1.78 (3H, s, eq. NAc), 1.92, 1.95 (3H each, both s, eq. OAc × 2), 3.32 (3H, s), 3.34, 3.37, 3.40, 3.42, 3.50 (6H each, all s) ($OCH_3 \times 11$), 4.96 (2H, br t, J = 11 Hz, 2,6-H_2), 5.17 (1H, br s, $W_{h/2} = 5$ Hz, anom. H in rhamnoside), 7.20 (1H, d, $J = 9$ Hz, exchangeable with D_2O, NH). FD-MS (m/z): 929 (M^+, 100%).

Methanolysis of 6a——A solution of **6a** (5 mg) in AcCl–MeOH (3 : 20, 1 ml) was heated under reflux for 4 h. Work-up of the reaction mixture as described above for **3a** gave a product, from which methyl 2,3,4-tri-*O*-methylrhamnopyranoside (**a**), methyl 2,3,4,6-tetra-*O*-methylglucopyranoside (**c**), and methyl 3,4,6-tri-*O*-methylgalactopyranoside (**d**) were identified by TLC and GLC comparisons as described above.

Lead Tetraacetate Oxidation Followed by Nitromethane Treatment of 7a——A solution of **7a** (480 mg) in benzene (30 ml) was treated with $Pb(OAc)_4$ (1.0 g) and the mixture was heated under reflux for 5 h. Work-up of the reaction mixture as described above for **3a** gave a product (486 mg, 95%),[6] which was dissolved in MeOH (3 ml) and CH_3NO_2 (10 ml). The solution was treated with 10% NaOMe–MeOH (3 ml) under an N_2 atmosphere and stirred at 33 °C for 3 d. The reaction mixture was worked up as described above for **3a** and the product was subjected to column chromatography (SiO_2 50 g, benzene–acetone = 30 : 1) to furnish **8** (184 mg, 85%) and a mixture of nitrocyclitol–oligosides (80 mg). **8** was shown to be identical with an authentic sample[10] by mixed mp, TLC (benzene–acetone = 10 : 1), and IR (KBr) comparisons. Purification of the nitrocyclitol-oligoside mixture by column chromatography (SiO_2 25 g, benzene–acetone = 3 : 1) twice and recrystallization of the product from ether furnished **9** (40 mg, 14%). **9**, mp 97—99 °C (colorless needles), $[\alpha]_D^{19}$ −37.8° (c = 0.45, $CHCl_3$). *Anal.* Calcd for $C_{26}H_{47}NO_{16}$: C, 49.60; H, 7.52; N, 2.22. Found: C, 49.49; H, 7.30; N, 2.23. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1568, 1373. ^{1}H-NMR (d_6-acetone, δ): 1.23 (3H, d, J = 6 Hz, *sec*-CH_3 in rhamnose), 3.36, 3.38, 3.41, 3.49, 3.51, 3.53, 3.59, 3.65 (3H each, all s, $OCH_3 \times 8$), 4.48 (1H, t, J = 10 Hz, $>CHNO_2$), 4.72 (1H, d, $J = 7$ Hz, anom. H in galactoside), 5.12 (1H, br s, $W_{h/2} = 5$ Hz, anom. H in rhamnoside).

Reduction Followed by Acetylation of 9 Giving 9a——A solution of **9** (18 mg) in EtOH (3 ml) was treated with a suspension of Raney Ni (T-4) in EtOH (1 ml) and the mixture was shaken under a hydrogen atmosphere at 26 °C for 4 h. Work-up of the reaction mixture as described for **3** gave a product, which was acetylated with Ac_2O–pyridine (1 : 1, 1 ml) at 30 °C with stirring for 15 h. Usual work-up followed by preparative TLC purification (benzene–acetone = 1 : 1) of the product furnished **9a** (15 mg, 72%). **9a**, mp 115—118 °C (colorless needles from EtOH), $[\alpha]_D^{17}$ −27.9° (c = 1.49, MeOH). *Anal.* Calcd for $C_{32}H_{55}NO_{17}$: C, 52.96; H, 7.64; N, 1.93. Found: C, 52.58; H, 7.63; N, 2.07. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1750, 1684, 1520, 1238. ^{1}H-NMR ($CDCl_3$, δ): 1.27 (3H, d, $J = 6$ Hz, *sec*-CH_3 in rhamnose), 1.90 (3H, s, eq. NAc), 2.04, 2.07 (3H each, both s, eq. OAc × 2), 3.41, 3.48, 3.50, 3.67 (3H each, all s), 3.46, 3.54 (6H each, both s) ($OCH_3 \times 8$), 4.68 (2H, br t, J = 10 Hz, 2,6-H_2), 5.21 (1H, br s, $W_{h/2} = 5$ Hz, anom. H in rhamnoside), 5.52 (1H, d, J = 10 Hz, exchangeable with D_2O, NH). ^{1}H-NMR (d_6-DMSO, δ): 1.22 (3H, d, $J = 6$ Hz, *sec*-CH_3 in rhamnose), 1.71 (3H, s, eq. NAc), 1.91, 1.97 (3H each, both s, eq. OAc × 2), 3.28 (12H, s), 3.33, 3.42 (6H each, both s) ($OCH_3 \times 8$), 5.01 (1H, br s, $W_{h/2} = 5$ Hz, anom. H in rhamnoside), 7.65 (1H, d, J = 10 Hz, exchangeable with D_2O, NH). FD-MS (m/z): 725 (M^+, 100%).

Methanolysis of 9a——A solution of **9a** (5 mg) in AcCl–MeOH (3 : 20, 1 ml) was heated under reflux for 4 h. Work-up of the reaction mixture as described for **3a** gave a product, from which methyl 2,3,4-tri-*O*-methylrhamnopyranoside (**a**) and methyl 3,4,6-tri-*O*-methylgalactopyranoside (**d**) were identified by TLC and GLC as described above.

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References and Notes

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13) The instruments used to obtain the physical data and the experimental conditions for chromatography were the same as those described in our previous paper.[10a)]
14) Compounds for which all attempts at crystallization were unsuccessful are described as white powder.
15) Under these GLC conditions, **a**, **b**, and **c** could not be identified.