SYNTHESIS OF D-ALLOSAN FROM LEVOGLUCOSENONE

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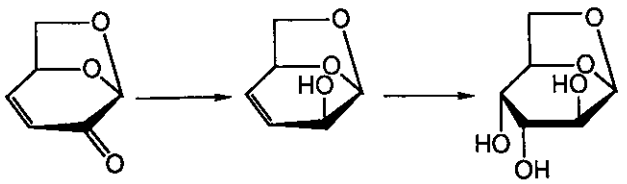
Abstract --- The stereoselective reduction and *cis*-dihydroxylation of levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose), gave D-allosan (1,6-anhydro-β-D-allopyranose) in high yield.

Levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose, **1**)[1] is a pyrolytic product of cellulose.[2] The structure of **1** is attractive as a starting material for a variety of organic syntheses because **1** includes convertible functional groups and two chiral centers. We have synthesized various useful compounds from **1** to date and demonstrated its great utility as a chiral building block.[3]

D-Allosan (**6**) is 1,6-anhydro sugar of D-allose. The structure of **6** is suitable as a starting material for syntheses of saccharides. However, the precedented reports afford **6** in low overall yield due to their low stereoselectivity.[4] Thus, more selective synthesis of **6** is required. In this paper, we describe a novel synthesis of D-allosan (1,6-anhydro-β-D-allopyranose, **6**) from **1**.

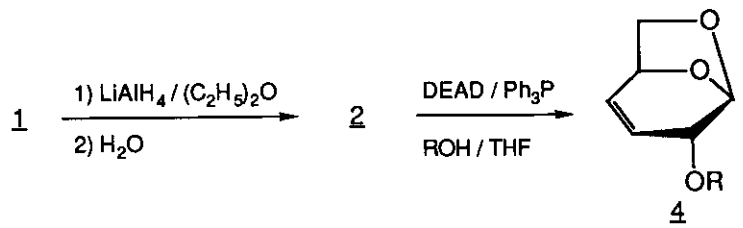
RESULTS AND DISCUSSION

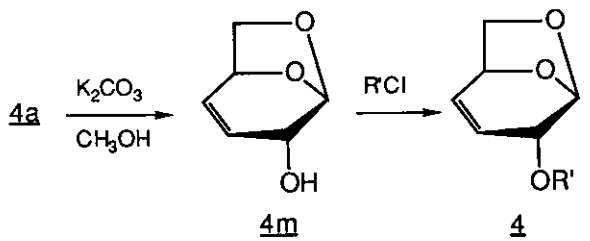
We have reported the synthesis of D-altrosan (**3**) by reduction of the carbonyl group of **1** and *cis*-dihydroxylation of the carbon-carbon double bond of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) (Scheme 1).[3e] D-Allosan (**6**) is the C-2 epimer of **3**. We anticipated that the inversion of the configuration of the hydroxyl group of **2** and *cis*-dihydroxylation of the carbon-carbon double bond of **4** would afford **6** (Scheme 2).

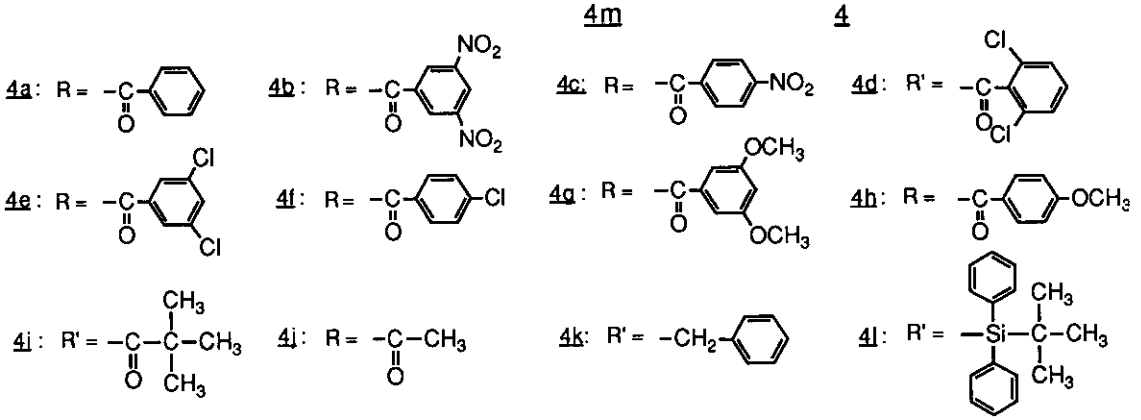


1 : Levoglucosenone 2 3

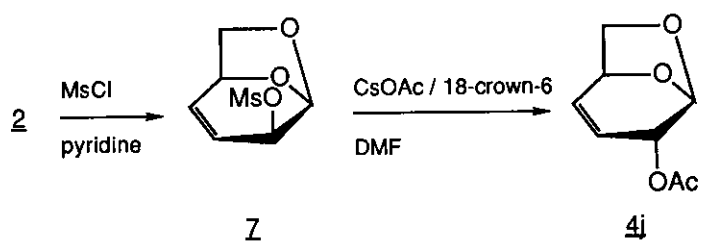
Scheme 1







Scheme 2



Scheme 3

The Reduction of **1**

The reduction of the carbonyl group of **1** with lithium aluminium hydride stereoselectively afforded **2** according to the previous papers.[2,3e,5]

Inversion of the Configration of the Hydroxyl Group of **2**

The inversion of the configuration of the hydroxy group of *threo*-form (**2**) afforded *erythro*-form (**4**) by Mitsunobu procedure[6] or with cesium carboxylate via the *O*-mesylation.[7]

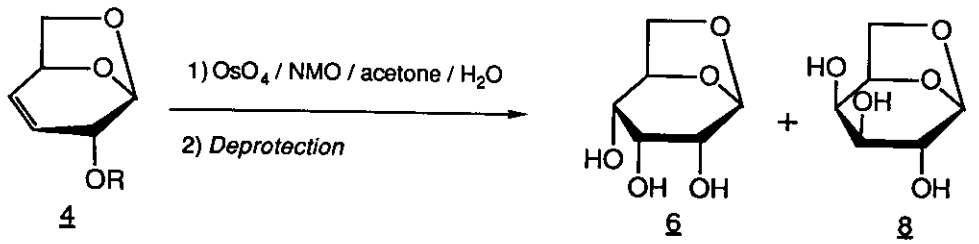
Treatment of **2** with carboxylic acid by Mitsunobu procedure afforded 2-*O*-acyl protected **4** (Scheme 2). Since we examined the effects of a protecting group of the allylic hydroxyl group on the 2-position of **4** in the next step (*cis*-dihydroxylation), we prepared various 2-*O*-acyl protected **4** (Scheme 3). Inversion with benzoic acid afforded **4a** in the best yield (91%) of **4**. Further, **4m** was afforded by cleavage of the benzoyl group of **4a** with potassium carbonate in methanol. **4d** and **4i** were obtained by *O*-acylation of **4m** with acyl chloride. **4k** was afforded by benzylation of **4m** with benzyl chloride. **4l** was given by silylation of **4m** with *tert*-butyldiphenylsilyl chloride.

We also examined the inversion of the configuration of the hydroxyl group on **2** by S_N2 type displacement with cesium carboxylate via the *O*-mesylation (Scheme 3).[7] *O*-Mesylation of **2** afforded **7** in 62.6% yield. Treatment of **7** with cesium acetate and 18-crown-6-ether in *N,N*-dimethylformamide gave **4j** in 68.8% yield.

cis-Dihydroxylation of Allylic Alcohol **4**

The *cis*-dihydroxylation of **4** with catalytic osmium tetroxide gives D-allosan and D-galactosan. In regard to the selectivity of the formation of D-allosan (**6**), we examined the effects of a protecting group of the allylic hydroxyl group on the 2-position of **4**,[8-10] using various protected compound (**4**). *cis*-Dihydroxylation of **4** with catalytic osmium tetroxide and *N*-methylmorpholine *N*-oxide in acetone-water and further cleavage of the protecting group of the product afforded a diastereomeric mixture of **6** and **8** (Scheme 4). Ratio of **6** : **8** was determined by ^{13}C-nmr spectral analysis of the mixture.[11]

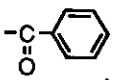
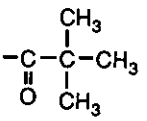
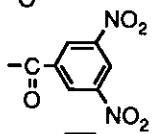
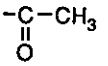
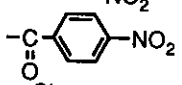
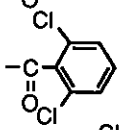
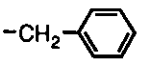
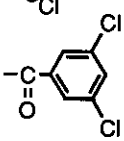
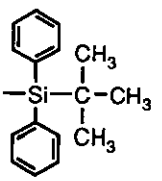
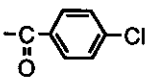
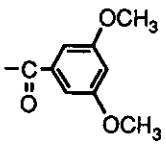
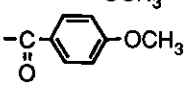
The results are summarized in Table 1. The *cis*-dihydroxylation of *O*-acyl-protected compounds (**4a-j**) gave higher *allo*-selectivities than those of **4k**, **4l**, and **4m**, having no carbonyl group. It is thought that this fact results from "osmiophilic carbonyl group". That is, a lone pair of electrons of the oxgen atom or π-bond of the carbonyl group of acyl group may preferetially attract electrophilic osmium tetroxide to the α-side on the pyranose ring. *Allo*-selectivities of benzoate derivatives (**4a-h**) were higher than those of pivaloate(**4i**)and acetate(**4j**), since the benzene ring possibly enhanced the electronic interactions between the carbonyl group and osmium tetroxide.[12] The kinds and positions of substituent groups on the benzene ring also affected *allo / galacto*



4 6 8

Scheme 4

Table 1. *cis*-Dihydroxylation of **4** with catalytic osmium tetroxide[a]

compound **4**	R	Slectivity[b] (*allo* (**6**) : *galacto* (**8**))	compound **4**	R	Slectivity[b] (*allo* (**6**) : *galacto* (**8**))
4a		7 : 1	**4i**		4 : 1
4b		only **6**	**4j**		3.5 : 1
4c		12 : 1			
4d		2 : 1	**4k**[c]		1 : 1
4e		9 : 1	**4l**		0.5 : 1
4f		8 : 1			
4g		10 : 1	**4m**	–H	2 : 1
4h		6 : 1			

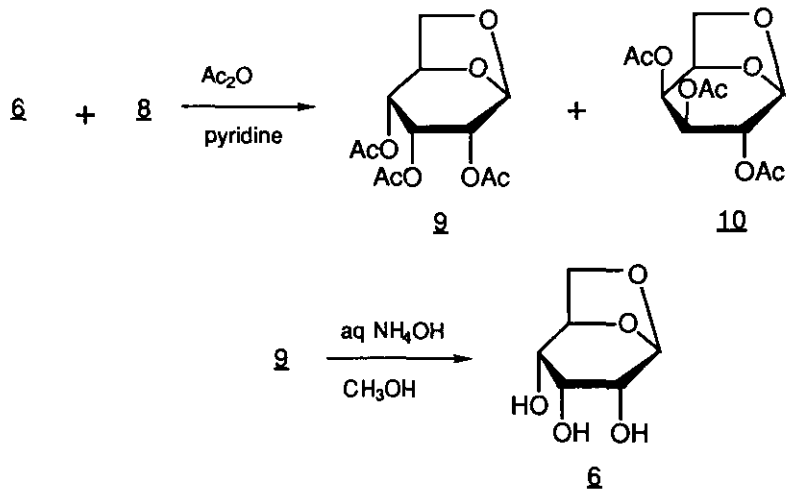
a) *cis*-Dihydroxylation was carried out under the following conditions; 2.0 mmol of **4**, 0.2 mmol of OsO_4 (in *tert*-butyl alcohol, 1 g / 30 ml), 4.0 mmol of *N*-methylmorpholine *N*-oxide, 10 ml of acetone-water (v/v = 8/1), room temperature, 20 h.[14] b) Determined by ^{13}C-nmr spectra. c) This is the ratio of 1,6-anhydro-2-*O*-benzyl-β-D-allopyranose to 1,6-anhydro-2-*O*-benzyl-β-D-galactopyranose, as determined by ^{13}C-nmr spectra in D_2O and CD_3OD (= 2 : 1).

selectivities. *cis*-Dihydroxylation of 3,5-dinitrobenzoate (**4b**) proceeded with α-side specificity to produce only **6**.

In previous reports, it was also described that the presence of osmiophilic functional groups derived stereoselective *cis*-dihydroxylation.[10,13]

The Separation of D-Allosan (**6**) and D-Galactosan (**8**).

The above mixture of D-allosan (**6**) and D-galactosan (**8**) could not be separated by column chromatography. Treatment of the mixture of **6** and **8** with acetic anhydride in pyridine, gave each of the corresponding triacetates (**9** and **10**). Pure 2,3,4-*O*-triacetyl-1,6-anhydro-β-D-allopyranose (**9**) was obtained easily by column chromatography in 77.4% yield (best yield, based on **4a**).[15] Treatment of **9** with ammonia water in methanol gave **6** in 91.6% yield.



Scheme 5

Conclusions:

We developed a method for preparing D-allosan (**6**) in 6 steps in 45.4% overall yield from levoglucosenone (**1**). In *cis*-dihydroxylation of the allylic alcohol (**4**), the acyl-protection of the allylic alcohol on the α-side facilitated diastereoselective attack on the carbon-carbon double bond by osmium tetroxide from the same α-side of the pyranose ring. That the carbonyl group of the acyl group may have been osmiophilic would be an explanation for this.

EXPERIMENTAL

Spectral Measurements.

All bps and mps were uncorrected. Ir spectra were measured on a Jasco FT/IR-5000 spectrophotometer. ^{1}H-Nmr spectra were recorded at 300 MHz and ^{13}C-nmr spectra at 75 MHz, with TMS as an internal standard on a Brucker AC-300P spectrometer. Optical rotation was measured on a Jasco DIP-370 polarimeter.

Inversion of 2 according to the Mitsunobu Procedure.

General Procedure.

To a stirred and ice-cooled mixed solution of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) (1 equiv.), triphenylphosphine (2 equiv.), and carboxylic acid (2 equiv.) in dry tetrahydrofuran (1.6 ml / mmol) was added dropwise a solution of diethylazodicarboxylate (2 equiv.) in dry tetrahydrofuran (1.6 ml / mmol) under a nitrogen atmosphere. The mixture was then stirred for *ca.* 2 days at room temperature under the same atmosphere, followed by evaporation under reduced pressure. The residue was filtered through silica gel using chloroform as the solvent to remove triphenylphosphine oxide. The filtrate was evaporated under reduced pressure and the product was isolated by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate) to obtain pure **4**.

1,6-Anhydro-2-*O*-benzoyl-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (4a).

To a stirred and ice-cooled mixed solution of 2.56 g (20.0 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**), 10.49 g (40.0 mmol) of triphenylphosphine, and 4.89 g (40.0 mmol) of benzoic acid in 32 ml of dry tetrahydrofuran was added dropwise a solution of 6.97 g (40.0 mmol) of diethyl azodicarboxylate in 32 ml of dry tetrahydrofuran under a nitrogen atmosphere. The mixture was stirred for 2 days at room temperature under the same atmosphere, followed by evaporation under reduced pressure. The residue was filtered through silica gel using chloroform as the solvent to remove triphenylphosphine oxide. The filtrate was evaporated under reduced pressure and the product was isolated by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 5-4/1;v/v) to obtain 4.23 g (91.1 %) of pure 1,6-anhydro-2-*O*-benzoyl-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4a**). This was recrystallized from *n*-hexane-ether (1/1,v/v).; mp 59.6-61.2°C; $[\alpha]_D^{27}$ -249° (*c* 0.31, $CHCl_3$); ir (KBr) 2900(w), 1717(s), 1601(w), 1456(m), 1394(w), 1319(m), 1247(s), 1168(w), 1102(s), 1071(m), 1048(w), 1023(s), 988(s), 905(s), 872(s), 801(m) and 710(s) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 8.11-8.07 (2H, m, aromatic H), 7.60-7.55 (1H, m, aromatic H), 7.47-7.41 (2H, m, aromatic H), 6.38 (1H, ddd, *J*=9.8, 4.7, and 1.1 Hz, H-4), 5.91 (1H, ddd, *J*=9.8, 3.8, and 1.9 Hz, H-3), 5.68 (1H, br, H-1), 5.01 (1H, m, H-2),

4.81 (1H, ddd, *J*=4.7, 4.7 and 0.7 Hz, H-5), 3.80-3.73 (2H, m, H-6 and H-6'); Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found C, 67.20; H, 5.13.

1,6-Anhydro-3,4-dideoxy-2-*O*-(3,5-dinitrobenzoyl)-β-D-*erythro*-hex-3-enopyranose (**4b**).

The inversion of **2** according to the Mitsunobu procedure using 3,5-dinitrobenzoic acid as a carboxylic acid gave 1,6-anhydro-3,4-dideoxy-2-*O*-(3,5-dinitrobenzoyl)-β-D-*erythro*-hex-3-enopyranose (**4b**) (yield; 84.1%). This was recrystallized from *n*-hexane-ether-chloroform (1/1/1,v/v/v).; mp 154.2-155.3°C; $[\alpha]_D^{25}$ -181° (*c* 0.30, $CHCl_3$); ir (KBr) 3106(m), 2896(w), 1736(s), 1630(m), 1543(s), 1462(w), 1348(s), 1270(s), 1166(m), 1125(w), 1081(w), 1021(w), 996(m), 915(m), 874(m), 822(w), 801(w), 774(w), 719(s), 455(w) and 437(w) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 9.26-9.19 (3H, m, aromatic H), 6.47 (1H, dd, *J*=9.9 and 4.7 Hz, H-4), 5.92 (1H, ddd, *J*=9.9, 3.8, and 2.0 Hz, H-3), 5.72 (1H, br, H-1), 5.07 (1H, d, *J*=3.8 Hz, H-2), 4.87 (1H, dd, *J*=4.7 and 4.7 Hz, H-5), 3.82-3.76 (2H, m, H-6 and H-6'); Anal. Calcd for $C_{13}H_{10}N_2O_8$: C, 48.46; H, 3.13; N, 8.69. Found C, 48.26; H, 3.14; N, 8.63.

1,6-Anhydro-3,4-dideoxy-2-*O*-(4-nitrobenzoyl)-β-D-*erythro*-hex-3-enopyranose (**4c**).

The inversion of **2** according to the Mitsunobu procedure using 4-nitrobenzoic acid as a carboxylic acid gave 1,6-anhydro-3,4-dideoxy-2-*O*-(4-nitrobenzoyl)-β-D-*erythro*-hex-3-enopyranose (**4c**) (yield; 75.1%). This was recrystallized from *n*-hexane-ether-chloroform (= 1/1/1,v/v/v).; mp 128.8-130.0°C; $[\alpha]_D^{24}$ -234° (*c* 1.00, $CHCl_3$); ir (KBr) 3428(w), 3112(w), 2958(w), 2906(w), 2348(w), 1949(w), 1719(s), 1601(m), 1520(s), 1412(w), 1396(w), 1352(s), 1323(s), 1270(s), 1166(m), 1116(s), 1102(s), 1019(s), 992(m), 973(m), 903(m), 880(s), 859(m), 801(m), 783(m), 717(s), 576(w) and 484(w) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 8.31-8.24 (4H, m, aromatic H), 6.42 (1H, ddd, *J*=9.8, 4.7 and 1.1 Hz, H-4), 5.91 (1H, ddd, *J*=9.8, 3.9, and 2.0 Hz, H-3), 5.69 (1H, br, H-1), 5.03 (1H, d, *J*=3.9 Hz, H-2), 4.85-4.82 (1H, m, H-5), 3.81-3.74 (2H, m, H-6 and H-6'); Anal. Calcd for $C_{13}H_{11}NO_6$: C, 56.32; H, 4.00; N, 5.05. Found C, 56.01; H, 3.97; N, 5.03.

1,6-Anhydro-2-*O*-(3,5-dichlorobenzoyl)-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4e**).

The inversion of **2** according to the Mitsunobu procedure using 3,5-dichlorobenzoic acid as a carboxylic acid gave 1,6-anhydro-2-*O*-(3,5-dichlorobenzoyl)-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4e**) (yield; 77.7%). This was recrystallized from *n*-hexane-ether-chloroform.; mp 102.5-103.1°C; $[\alpha]_D^{20}$ -194° (*c* 1.00, $CHCl_3$); ir (KBr) 3072(w), 2974(w), 2890(w), 2364(w), 2344(w), 1717(s), 1572(s), 1437(m), 1396(w), 1352(w), 1323(w), 1263(s), 1145(m), 1127(m), 1104(m), 1081(w), 1023(s), 1002(s), 969(m), 909(s), 884(s), 868(s), 803(s), 762(s), 719(w), 704(w), 659(w), 574(w), 478(w), and 418(w) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 7.95-7.94 (2H, m, aromatic H), 7.56-7.55 (1H, m, aromatic H), 6.40 (1H, dd, *J*=9.8 and 4.7 Hz, H-4), 5.88 (1H, dddd,

J=9.8, 3.8, 2.0, and 0.7 Hz, H-3), 5.66 (1H, br, H-1), 4.98 (1H, d, *J*=3.8 Hz, H-2), 4.84-4.81 (1H, m, H-5), 3.80-3.73 (2H, m, H-6 and H-6'); Anal. Calcd for $C_{13}H_{10}O_4Cl_2$: C, 51.85; H, 3.35; Cl, 23.55. Found C, 51.66; H, 3.28; Cl, 23.69.

1,6-Anhydro-2-*O*-(4-chlorobenzoyl)-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4f**).

The inversion of **2** according to the Mitsunobu procedure using 4-chlorobenzoic acid as a carboxylic acid gave 1,6-anhydro-2-*O*-(4-chlorobenzoyl)-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4f**) (yield; 84.3%).; n_D^{20} 1.56°; $[\alpha]_D^{24}$ -235° (*c* 1.08, $CHCl_3$); ir (KBr) 4082(w), 3422(w), 3096(w), 3054(w), 2570(w), 2370(w), 2100(w), 1928(w), 1721(s), 1597(s), 1491(s), 1404(m), 1350(m), 1323(m), 1267(s), 1172(m), 1104(s), 1048(m), 1017(s), 996(s), 969(s), 936(m), 907(s), 878(s), 851(m), 801(s), 760(s), 723(m), 708(m), 685(m), 629(w), 598(w), 576(w), 528(s), 478(s), and 453(w) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 8.04-7.99 (2H, m, aromatic H), 7.44-7.39 (2H, m, aromatic H), 6.38 (1H, ddd, *J*=9.8, 4.7 and 1.1 Hz, H-4), 5.89 (1H, ddd, *J*=9.8, 3.9, and 1.9 Hz, H-3), 5.54 (1H, br, H-1), 4.99 (1H, m, H-2), 4.83-4.80 (1H, m, H-5), 3.79-3.73 (2H, m, H-6 and H-6'); Anal. Calcd for $C_{13}H_{11}O_4Cl$: C, 58.55; H, 4.16; Cl, 13.29. Found C, 58.42; H, 4.15; Cl, 13.29.

1,6-Anhydro-3,4-dideoxy-2-*O*-(3,5-dimethoxybenzoyl)-β-D-*erythro*-hex-3-enopyranose (**4g**).

The inversion of **2** according to the Mitsunobu procedure using 3,5-dimethoxybenzoic acid as a carboxylic acid gave 1,6-anhydro-3,4-dideoxy-2-*O*-(3,5-dimethoxybenzoyl)-β-D-*erythro*-hex-3-enopyranose (**4g**) (yield; 83.7%). This was recrystallized from *n*-hexane-ether.; mp 55.7-60.5°C; $[\alpha]_D^{21}$ -167° (*c* 1.03, $CHCl_3$); ir (KBr) 3052(w), 3010(w), 2984(m), 2960(m), 2900(m), 2844(w), 1713(s), 1601(s), 1473(s), 1429(m), 1357(s), 1323(m), 1305(s), 1228(s), 1209(s), 1162(s), 1125(m), 1100(m), 1071(m), 1046(s), 1019(s), 1000(s), 975(m), 928(w), 905(m), 874(s), 835(m), 801(m), 758(s), 723(m), 706(m), 669(m), 596(w), 576(w), 542(w), 497(w), 478(m), and 439(w) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 7.22 (2H, d, *J*=2.4 Hz, aromatic H), 6.66 (1H, dd, *J*=2.4 and 2.4 Hz, aromatic H), 6.38 (1H, ddd, *J*=9.8, 4.7 and 1.2 Hz, H-4), 5.90 (1H, ddd, *J*=9.8, 3.8, and 1.9 Hz, H-3), 5.68 (1H, br, H-1), 4.98 (1H, d, *J*=3.8 Hz, H-2), 4.83-4.80 (1H, m, H-5), 3.88-3.72 (8H, m, H-6, H-6', and CH_3O); Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found C, 61.53; H, 5.37.

1,6-Anhydro-3,4-dideoxy-2-*O*-(4-methoxybenzoyl)-β-D-*erythro*-hex-3-enopyranose (**4h**).

The inversion of **2** according to the Mitsunobu procedure using 3,5-dimethoxybenzoic acid as a carboxylic acid gave 1,6-anhydro-3,4-dideoxy-2-*O*-(4-methoxybenzoyl)-β-D-*erythro*-hex-3-enopyranose (**4h**) (yield; 78.5%). This was recrystallized from *n*-hexane-ether.; mp 58.5-64.5°C; $[\alpha]_D^{23}$ -240° (*c* 0.99, $CHCl_3$); ir (KBr) 2984(w), 2890(w), 2840(w), 2348(w), 1709(s), 1607(s), 1578(w), 1514(m), 1460(w), 1423(w), 1398(w), 1354(w), 1328(m), 1267(s), 1170(s), 1127(m), 1100(s), 1050(w), 1023(s), 994(s), 967(m), 930(w), 907(m), 874(m),

845(m), 801(m), 770(m), 721(m), 696(m), 634(w), 619(w), 594(w), 565(w), 511(w), and 482(m) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 8.08-8.01 (2H, m, aromatic H), 6.97-6.90 (2H, m, aromatic H), 6.38 (1H, ddd, *J*=9.8, 4.7 and 0.6 Hz, H-4), 5.91 (1H, ddd, *J*=9.8, 3.9, and 1.9 Hz, H-3), 5.69 (1H, br, H-1), 5.00 (1H, m, H-2), 4.82 (1H, ddd, *J*=4.7, 4.1, and 0.6 Hz, H-5), 3.88 (3H, s, CH_3O), 3.81-3.74 (2H, m, H-6 and H-6'); Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found C, 64.10; H, 5.25.

2-*O*-Acetyl-1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4j**).

The inversion of **2** according to the Mitsunobu procedure using acetic acid as a carboxylic acid gave 2-*O*-acetyl-1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4j**). This was distilled under reduced pressure (bp_2 93-94 °C) (yield; 51.2%).; n_D^{22} 1.48°; $[\alpha]_D^{28}$ -257° (*c* 1.01, $CHCl_3$); ir (KBr) 2962(m), 2898(m), 1731(s), 1475(w), 1435(w), 1375(s), 1230(s), 1168(m), 1127(s), 1083(m), 1021(s), 1002(s), 973(s), 911(s), 884(s), 868(s), 801(s), 762(w), 712(m), 658 (m), 609(m), 590(w), 578(w), 545(m), 513(w), 499(w), 484(m), 458(w), 435(w), 426(m), and 414(w) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 6.33 (1H, ddd, *J*=9.8, 4.7 and 1.1 Hz, H-4), 5.79 (1H, ddd, *J*=9.8, 3.8, and 1.9 Hz, H-3), 5.55 (1H, br, H-1), 4.78-4.75 (2H, m, H-2 and H-5), 3.75-3.69 (2H, m, H-6 and H-6'), 2.11 (3H, s, Ac); Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found C, 56.33; H, 6.01.

1,6-Anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4m**).

A solution of 1.39 g (6.00 mmol) of 1,6-anhydro-2-*O*-benzoyl-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4a**) and 4.16 g (30.1 mmol) of potassium hydrogen carbonate in 1072 ml of methanol was stirred for 1.5 h at room temperature. The reaction mixture was evaporated under reduced pressure and the precipitated potassium salt was filtered off. The filtrate was evaporated under reduced pressure. The product was isolated by column chromatography on silica gel (eluent: *n*-hexane / diethyl ether = 1/1; v/v) to give 0.76 g (98.6 %) of pure 1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4m**) as white powder. This was recrystallized from *n*-hexane-ether (1/1,v/v).; mp 59.0-60.2°C; $[\alpha]_D^{25}$ -240° (*c* 1.01, $CHCl_3$)(lit.,[16] mp 53-54°C; $[\alpha]_D^{23}$ -236°, *c* 1.00, $CHCl_3$); ir (KBr) 3500(br), 3056(w), 2990(m), 2962(s), 2902(m), 1475(w), 1412(w), 1363(w), 1292(m), 1253(m), 1164(m), 1125(s), 1052(s), 1015(s), 982(m), 965(m), 922(s), 893(s), 866(m), 853(m), 799(m), 733(m), 706(m), 594(w), 574(w), 565(w), 557(w), 543(w), 514(w), 501(w), 480(m), 460(m), 429(w), and 410(m) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 6.19 (1H, ddd, *J*=9.8, 4.7, and 0.9 Hz, H-4), 5.83 (1H, ddd, *J*=9.8, 4.0, and 2.0 Hz, H-3), 5.53 (1H, dd, *J*=2.0 and 1.8 Hz, H-1), 4.71-4.68 (1H, m, H-5), 3.72-3.62 (3H, m, H-2, H-6, and H-6'), 1.85 (1H, d, *J*=16.9 Hz, OH); Anal. Calcd for $C_6H_8O_3$: C, 56.25; H, 6.29. Found C, 56.39; H, 6.34.

1,6-Anhydro-2-*O*-(2,6-dichlorobenzoyl)-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4d**).

A solution of 0.97 g (7.59 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4m**) and 4.77 g (22.8 mmol) of 2,6-dichlorobenzoyl chloride in 50 ml of pyridine was stirred for 3 h at 60-70 °C, and stirred for 9 h at room temperature. The reaction mixture was evaporated under reduced pressure, poured into ice-water, and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was distilled off under reduced pressure. The product was isolated by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 5/1; v/v) to give 2.21 g (96.9 %) of pure 1,6-anhydro-2-*O*-(2,6-dichlorobenzoyl)-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4d**) as white powder. This was recrystallized from *n*-hexane-ether-chloroform.; mp 143.6-144.5°C; $[\alpha]_D^{22}$ -174° (*c* 1.00, $CHCl_3$); ir (KBr) 3404(br), 3078(w), 3018(w), 2964(m), 2900(m), 1736(s), 1566(m), 1437(m), 1365(w), 1348(w), 1265(s), 1197(w), 1143(s), 1085(m), 1056(m), 1021(m), 990(s), 963(m), 930(m), 907(m), 878(s), 781(m), 745(m), 690(w), 598(w), 576(w), 484(m), 445(w), and 412(w) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 7.34-7.25 (3H, m, aromatic H), 6.40 (1H, ddd, *J*=9.8, 4.7 and 1.1 Hz, H-4), 5.92 (1H, ddd, *J*=9.8, 3.9, and 2.0 Hz, H-3), 5.73 (1H, br, H-1), 5.12 (1H, m H-2), 4.81-4.78 (1H, m, H-5), 3.80-3.73 (2H, m, H-6 and H-6'); Anal. Calcd for $C_{13}H_{10}O_4Cl_2$: C, 51.85; H, 3.35; Cl, 23.55. Found C, 51.48; H, 3.32; Cl, 23.69.

1,6-Anhydro-3,4-dideoxy-2-*O*-pivaloyl-β-D-*erythro*-hex-3-enopyranose (**4i**).

A solution of 1.28 g (10.0 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4m**) and 3.62 g (30.0 mmol) of pivaloyl chloride in 100 ml of pyridine was stirred for 2.5 h at 60-70 °C, and stirred for 17.5 h at room temperature. The reaction mixture was evaporated under reduced pressure, poured into ice-water and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was distilled off under reduced pressure. The product was isolated by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 5/1; v/v), followed by distillation under reduced pressure ($bp_{0.22}$ 79-83 °C) to give 2.00 g (94.0 %) of pure 1,6-anhydro-3,4-dideoxy-2-*O*-pivaloyl-β-D-*erythro*-hex-3-enopyranose (**4i**) as a colorless oil; n_D^{22} 1.46°; $[\alpha]_D^{25}$ -224° (*c* 1.08, $CHCl_3$); ir (KBr) 2874(m), 2360(w), 1727(s), 1543(w), 1483(m), 1396(m), 1365(m), 1278(m), 1151(s), 1023(s), 1000(s), 907(m), 884(m), 864(m), 801(m), 772(w), 725(w), 710(w), 582(w), 563(w), 464(w), 426(s), and 408(s) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 6.31 (1H, ddd, *J*=9.8, 4.7 and 1.2 Hz, H-4), 5.76 (1H, ddd, *J*=9.8, 3.8, and 1.9 Hz, H-3), 5.50 (1H, br, H-1), 4.78-4.73 (2H, m, H-2 and H-5), 3.74-3.68 (2H, m, H-6 and H-6'), 1.22 (9H, s, *t*-butyl); ms *m/z* 213 ($(M+H)^+$); Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found C, 62.39; H, 7.39.

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4k**).

To a stirred and ice-cooled solution of 6 ml of dimethyl sulfoxide was slowly added 0.22 g (9.00 mmol) of sodium hydride in oil (abt. 50%). To this solution, 0.77 g (6.00 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4m**) in 3 ml of dimethyl sulfoxide was added dropwise with stirring, followed by ice-cooling under a nitrogen atmosphere, and stirring for 1 h at room temperature. To this solution, 1.52 g (12.0 mmol) of benzyl chloride was added dropwise and stirred for 1.5 h at room temperature. The reaction mixture was poured into 45 ml of ice-water, and extracted with ether. The organic layer was dried over anhydrous magnesium sulfate, and the solvent distilled off under reduced pressure. The product was isolated by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 4-3/1; v/v) and distilled under reduced pressure ($bp_{0.3}$ 122-125 °C) to afford 1.22 g (93.2 %) of pure 1,6-anhydro-2-*O*-benzyl-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4k**) as a colorless oil; n_D^{23} 1.55°; $[\alpha]_D^{23}$ -175° (*c* 1.02, $CHCl_3$); ir (KBr) 3034(m), 2960(m), 2890(m), 1497(m), 1456(m), 1390(m), 1365(m), 1301(m), 1247(w), 1166(m), 1125(s), 1073(s), 1044(s), 1021(s), 992(s), 922(m), 897(m), 870(s), 797(m), 739(m), 698(m), 613(w), and 476(m) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 7.38-7.27 (5H, m, aromatic H), 6.24 (1H, ddd, *J*=9.8, 4.7 and 1.3 Hz, H-4), 5.80 (1H, ddd, *J*=9.8, 3.8, and 2.0 Hz, H-3), 5.61 (1H, br, H-1), 4.73 (1H, ddd, *J*=4.7, 4.7 and 2.4 Hz, H-5), 4.67 (2H, S, PhC$\underline{H_2}$O), 3.67 (2H, d, *J*=2.4 Hz, H-6 and H-6'); Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found C, 71.20; H, 6.58.

1,6-Anhydro-2-*O*-(*tert*-butyldiphenylsilyl)-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4l**).

To a stirred and ice-cooled mixed solution of 0.77 g (6.01 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4m**) and 0.45 g (6.61 mmol) of imidazole in 4.5 ml of dry *N,N*-dimethylformamide was added dropwise 1.82 g (6.61 mmol) of *tert*-butyldiphenylsilyl chloride, followed by stirring for 3 h at room temperature. The reaction mixture was poured into ice-water, and extracted with ether. The organic layer was dried over anhydrous magnesium sulfate, and the solvent distilled off under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 5-4/1; v/v) to quantitatively afford 2.20 g of pure 1,6-anhydro-2-*O*-(*tert*-butyldiphenylsilyl)-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4l**).; n_D^{21} 1.51°; $[\alpha]_D^{25}$ -102° (*c* 1.01, $CHCl_3$); ir (KBr) 3442(br), 3074(s), 3050(s), 2934(s), 2892(s), 2862(s), 1966(w), 1895(w), 1829(w), 1740(m), 1661(w), 1591(m), 1570(w), 1473(s), 1429(s), 1392(s), 1363(m), 1317(m), 1245(m), 1189(m), 1168(m), 1075(br), 1040(s), 1023(s), 988(m), 969(m), 930(m), 897(m), 870(s), 845(s), 822(s), 793(m), 743(m), 702(s), 613(s), 578(w), 530(m), 505(s), and 433(m) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ: 7.73-7.67 (6H, m, aromatic H), 7.44-7.36 (4H, m, aromatic H), 6.09 (1H, ddd, *J*=9.8, 4.8 and 1.0 Hz, H-4), 5.55 (1H, ddd, *J*=9.8, 3.7, and 2.0 Hz, H-3), 5.42 (1H, br, H-1), 4.69 (1H, dd, *J*=4.4 and

4.2 Hz, H-5), 3.68 (1H, d, *J*=3.7 Hz, H-2), 3.60-3.53 (2H, m, H-6 and H-6'), 1.08 (9H, s, *tert*-butyl); ms *m/z* 366 (M^+).

Inversion of **2** with cesium acetate.

1,6-Anhydro-2-*O*-mesyl-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (7).

To a stirred and ice-cooled solution of 0.25 g (1.98 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) in 2.0 ml of dry pyridine was added dropwise 0.34 g (3.00 mmol) of mesyl chloride under an nitrogen atmosphere followed by stirring for 3.5 h at 0°C. The reaction mixture was neutralized with 1 mol dm^{-1} hydrochloric acid and extracted with ether. The organic layer was washed with aqueous saturated sodium hydrocarbonate and then aqueous sodium chloride. It was dried over anhydrous magnesium sulfate and the solvent distilled off under reduced pressure. The residue was purified by recrystallization from *n*-hexane-ether-ethyl acetate (= 5/5/2,v/v) to afford 0.26 g (62.6%) of 1,6-anhydro-2-*O*-mesyl-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**7**).; ^{1}H-nmr ($CDCl_3$) δ: 6.29 (1H, ddd, *J*=10.4, 4.3 and 1.3 Hz, H-4), 5.74-5.69 (2H, m, , H-2 and H-3), 5.44 (1H, br, H-1), 4.72 (1H, dd, *J*=4.3 and 4.2 Hz, H-5), 4.00 (1H, d, *J*=6.7 Hz, H-6), 3.84 (2H, ddd, *J*=6.7, 4.2 and 1.3 Hz, H-6'), 3.13 (3H, s, mesyl).

Conversion of **7** to **4j**.

A reaction mixture of 0.21 g (1.00 mmol) of 1,6-anhydro-2-*O*-mesyl-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**7**), 0.58 g (3.00 mmol) of anhydrous cesium acetate and 0.26 g (1.00 mmol) of 18-crown-6 in 10 ml of *N,N*-dimethylformamide was stirred for 19 h at 120°C. After cooling, it was extracted with chloroform. The chloroform solution was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 4-3/1;v/v) to afford 0.12 g (68.8 %) of 2-*O*-acetyl-1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4j**) as a colorless oil. The ^{1}H-nmr spectral data of the oil was identical with those of **4j** obtained by the Mitsunobu procedure.

2,3,4-*O*-Triacetyl-1,6-anhydro-β-D-allopyranose (**9**).

a) Dihydroxylation: A solution (1.5 ml) of osmium tetroxide in *tert*-butyl alcohol (osmium tetroxide / *tert*-butyl alcohol = 1/30;w/v) was added to 2.00 mmol of a mixture of **4** and 0.47 g (4.00 mmol) of *N*-methylmorpholine *N*-oxide in acetone-water (10 ml, 8/1;v/v), and stirred for 20 h at room temperature. A 45 % aqueous sodium pyrosulfite solution (6 ml) was added to the reaction mixture with ice-cooling, and then the mixture was vigorously stirred for 10 min at room temperature. The reaction mixture was evaporated under reduced pressure. The residue was washed by hot ethanol and chloroform, and filtered. The filtrate was evaporated under reduced pressure.

b) Removal of Protecting Group: Removal of the protecting group was carried out with 25 % ammonia in methanol and stirring at room temperature overnight.[17] The reaction mixture was evaporated and dried under reduced pressure. The ratio of the products (**6** and **8**) was determined based on integration of the intensity of the carbons in the 75 MHz ^{13}C-nmr spectrum (D_2O).

c) Acetylation: To the above residue was added 20 ml of acetic anhydride and 100 ml of dry pyridine. The reaction mixture was stirred for *ca.* 3-6 h at 60-70 °C under a nitrogen atmosphere and then stirred overnight at room temperature. The mixture was evaporated under reduced pressure. The residue was poured into ice-water and extracted with chloroform three times. The organic layer was dried over anhydrous magnesium sulfate and the solvent was distilled off under reduced pressure. The separation of two isomers (**9** and **10**) from the residue by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 3-1/1; v/v) afforded 2,3,4-*O*-triacetyl-1,6-anhydro-β-D-galactopyranose (**10**) and 2,3,4-*O*-triacetyl-1,6-anhydro-β-D-allopyranose (**9**).

Conversion of **4a** to **9**.

A solution (1.5 ml) of osmium tetroxide in *tert*-butyl alcohol (osmium tetroxide / *tert*-butyl alcohol = 1/30;w/v) was added to a mixture of 0.46 g (2.00 mmol) of 1,6-anhydro-2-*O*-benzoyl-3,4-dideoxy-β-D-*erythro*-hex-3-enopyranose (**4a**) and 0.47 g (4.00 mmol) of *N*-methylmorpholine *N*-oxide in acetone-water (10 ml, 8/1;v/v), and stirred for 20 h at room temperature. A 45 % aqueous sodium pyrosulfite solution (6 ml) was added to the reaction mixture with ice-cooling, and then the mixture was vigorously stirred for 10 min at room temperature. The reaction mixture was evaporated under reduced pressure. The residue was washed by hot ethanol and chloroform and filtered. The filtrate was evaporated under reduced pressure. To the residue was added 20 ml of 25 % ammonia and 140 ml of methanol, followed by stirring at room temperature overnight. The reaction mixture was evaporated and dried under reduced pressure. The ratio of the products (**6** and **8**) was determined based on the intensity of the carbons in the 75 MHz ^{13}C-nmr spectrum (D_2O). To the residue was added 20 ml of acetic anhydride and 100 ml of dry pyridine. The mixture was stirred for 3 h at 60-70 °C under a nitrogen atmosphere, and then stirred overnight at room temperature. The mixture was evaporated under reduced pressure. The residue was poured into ice-water and extracted with chloroform three times. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was distilled off under reduced pressure. Two isomers (**9** and **10**) from the residue were separated by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 3-1/1; v/v). The first fraction gave 0.07 g (11.8%) of pure 2,3,4-*O*-triacetyl-1,6-anhydro-β-D-galactopyranose (**10**),[18] and the second, 0.45 g (77.4%) of pure 2,3,4-*O*-triacetyl-1,6-anhydro-β-D-allopyranose (**9**). **9** was recrystallized from *n*-hexane-diethyl ether respectively as a white powder.

2,3,4-*O*-Triacetyl-1,6-anhydro-β-D-galactopyranose (**10**); ^{1}H-nmr[10,19] ($CDCl_3$) δ: 5.35 (1H, d, *J*=3.0 Hz, H-1), 5.16-5.14 (2H, m, H-3 and H-4), 4.66 (1H, dd, *J*=3.0 and 1.4 Hz H-2), 4.40 (1H, br, H-5), 4.26 (1H, dd, *J*=7.5 and 3.9 Hz, H-6), 3.68-3.63 (1H, m, H-6'), 2.06 (6H, s, Ac), 1.96 (3H, s, Ac).

2,3,4-*O*-Triacetyl-1,6-anhydro-β-D-allopyranose (**9**); mp 86.4-87.2°C; $[\alpha]_D^{28}$ -73.8° (*c* 0.30, $CHCl_3$)(lit.,[4a] mp 88-89°C; $[\alpha]_D^{20}$ -70.8°, *c* 1, $CHCl_3$); ir (KBr) 1734(s), 1439(w), 1375(m), 1261(s), 1228(s), 1133(s), 1062(m), 1011(m), 975(w), 926(w), 899(m), 785(w), 739(w), 679(w), 617(w), 598(w), and 505(w) cm^{-1}; ^{1}H-nmr ($CDCl_3$)[10] δ: 5.52 (1H, d, *J*=2.5 Hz, H-1), 5.27 (1H, dd, *J*=4.8 and 4.7 Hz, H-3), 5.17-5.10 (2H, m, H-2 and H-4), 4.69 (1H, ddd, *J*=5.5, 2.5, and 0.8 Hz, H-5), 3.95 (1H, dd, *J*=8.3 and 0.8 Hz, H-6), 3.83 (1H, dd, *J*=8.3 and 5.5 Hz, H-6'), 2.19 (3H, s, Ac), 2.17 (3H, s, Ac), 2.00 (3H, s, Ac); Anal. Calcd for $C_{12}H_{16}O_8$: C, 50.00; H, 5.60. Found C, 49.99; H, 5.59.

1,6-Anhydro-β-D-allopyranose (D-Allosan; 6).

A solution of 0.58 g (2.00 mmol) of **9** in 10 ml of 25 % ammonia and 70 ml of methanol was stirred for 15 h at room temperature. The precipitate was filtered off and washed with methanol. The filtrate was evaporated under reduced pressure. The residue was purified by recrystallization from *iso*-propyl alcohol to afford 0.26 g (91.6%) of 1,6-anhydro-β-D-allopyranose (D-allosan;**6**); mp 174-176°C; $[\alpha]_D^{25}$ -76.5° (*c* 0.20, H_2O)(lit.,[4a] mp 178.5-180°C; $[\alpha]_D^{20}$ -75.8°, *c* 0.6, H_2O); ir (KBr) 3400(br), 1630(br), 1402(w), 1338(w), 1133(s), 1108(s), 1029(w), 998(w), 971(s), 946(m), 915(m), 857(m), 779(m), and 652(w) cm^{-1}; ^{1}H-nmr (D_2O, ppm from OD; 4.60 ppm) δ: 5.32 (1H, d, *J*=2.5 Hz, H-1), 4.50 (1H, dd, *J*=5.4 and 2.6 Hz, H-5), 3.70-3.54 (4H, m, H-2, H-3, H-4, and H-6); ^{13}C-nmr[11] (D_2O, ppm from 1,4-dioxane; 67.4 ppm) δ: 101.7(C-1), 76.9(C-5), 70.4(C-2), 70.3(C-4), 65.5(C-6), 63.7(C-3); Anal. Calcd for $C_6H_{10}O_5$: C, 44.45; H, 6.22. Found C, 44.33; H, 6.39.

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18. The deacetylation of **10** according to the above procedure afforded 1,6-anhydro-β-D-galactopyranose (D-galactosan; **8**)(yield; 59.0%); mp 201.2-205.0°C; $[\alpha]_D^{24}$ -23.2° (*c* 0.41, H_2O); ir (KBr) 3400(br), 1133(m), 1054(s), 1000(w), 969(w), 934(m), and 855(w) cm^{-1}; ^{1}H-nmr (D_2O, ppm from OD; 4.60 ppm) δ: 5.19 (1H, br, H-1), 4.29 (1H, dd, *J*=4.6 and 4.6 Hz, H-5), 4.10 (1H, d, *J*=7.6 Hz, H-6), 3.84 (1H, dd, *J*=4.6 and 4.6 Hz, H-4), 3.74-3.71 (1H, m, H-3), 3.59 (1H, br, H-2), 3.44 (1H, dd, *J*=7.3 and 5.4 Hz, H-6'); ^{13}C-nmr[11](D_2O, ppm from 1,4-dioxane; 67.4 ppm) δ: 101.5(C-1), 75.1(C-5), 72.1(C-2), 70.9(C-3), 65.0(C-4), 64.3(C-6); Anal. Calcd for $C_6H_{10}O_5$: C, 44.45; H, 6.22. Found C, 44.29; H, 6.57.

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