SYNTHESIS OF 1,6:3,4-DIANHYDRO-β-D-TALOPYRANOSE FROM LEVOGLUCOSENONE : EPOXIDATION OF OLEFIN *VIA trans*-IODOACETOXYLATION

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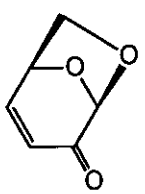
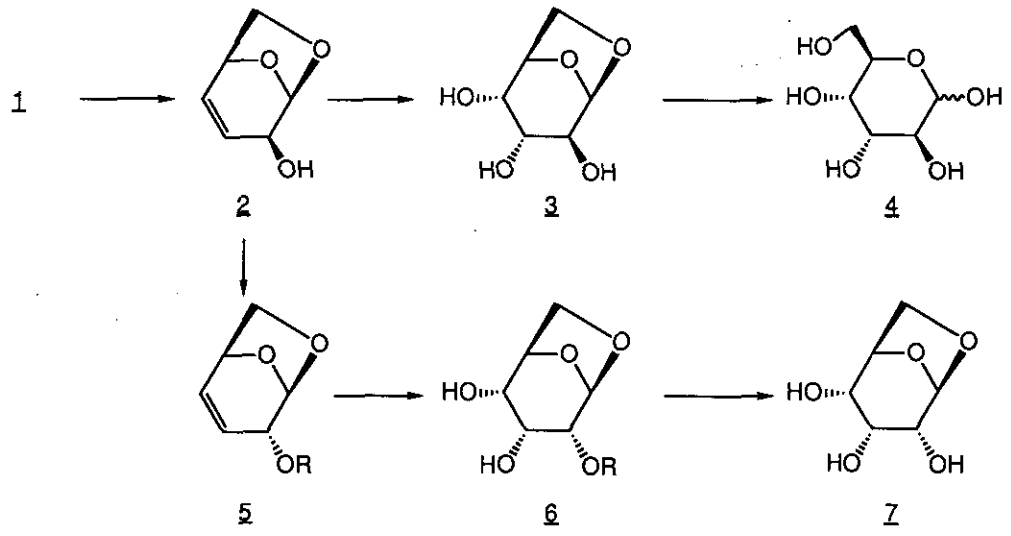
Abstract --- Levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose, **1**) was converted to give 1,6:3,4-dianhydro-β-D-talopyranose (**8**) in good yield through stereoselective *trans*-iodoacetoxylation followed by basic hydrolysis.

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 it 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]



1 : Levoglucosenone

In previous reports, D-altrosan (1,6-anhydro-β-D-altropyranose, **3**), D-altrose (**4**)[3e] and D-allosan (1,6-anhydro-β-D-allopyranose, **7**)[3f] were synthesized starting from **1** via the stereoselective *cis*-dihydroxylation of the C-C double bond of allylic alcohol (**2**) and (**5**) using osmium tetroxide as an oxidizing reagent (Scheme 1). During the investigation of the synthesis of rare sugars, we became interested in the Prévost-Woodward *cis*-dihydroxylation of **2**, because it is believed generally that Prévost-Woodward *cis*-dihydroxylation gives the sterically hindered *cis*-glycol preferentially. In this paper, we describe the unusual result obtained by that attempt.

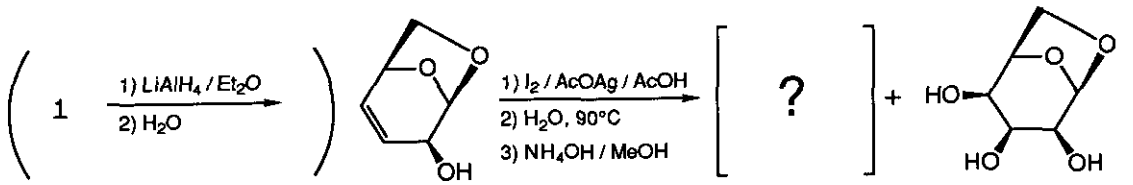


Scheme 1

Prévost-Woodward *cis*-dihydroxylation of allylic alcohol (**2**).

Allylic alcohol (**2**), which is easily obtained by the reduction of levoglucosenone (**1**),[2,3e] was examined under reaction conditions originally reported by Woodward.[4] That is, **2** was treated by iodine and silver acetate in dry acetic acid, followed by heating in the presence of water. The reaction mixture was neutralized, followed by treatment with ammonia in methanol in order to remove the acetyl group. After these procedures, two products were obtained. These were separated easily by column chromatography. The polar and minor one (18% yield) was D-talosan (1,6-anhydro-β-D-talopyranose, **9**),[5] which was expected from typical Prévost-Woodward *cis*-dihydroxylation. On the other hand, the structure of the less polar and main product (62% yield) was unknown

at this stage. Fortunately, the product was crystalline, and X-ray analysis confirmed its structure as 1,6:3,4-dianhydro-β-D-talopyranose (**8**).



2 8 9

Scheme 2

Table 1 Interatomic distances (Å) and angles (°) with e.s.d.'s in ( ).

O(1)	-	C(1)	1.444	(7)	C(1)	-	H(3)	1.102			
O(1)	-	C(6)	1.442	(7)	C(2)	-	C(3)	1.500	(1)		
O(2)	-	C(2)	1.451	(7)	C(2)	-	H(4)	1.128			
O(2)	-	C(6)	1.377	(8)	C(3)	-	C(4)	1.470	(1)		
O(3)	-	C(3)	1.478	(9)	C(3)	-	H(5)	1.174			
O(3)	-	C(4)	1.449	(7)	C(4)	-	C(5)	1.498	(8)		
O(4)	-	C(5)	1.404	(8)	C(4)	-	H(6)	1.228			
O(4)	-	H(1)	0.830	(6)	C(5)	-	C(6)	1.540	(1)		
C(1)	-	C(2)	1.498	(9)	C(5)	-	H(7)	1.015			
C(1)	-	H(2)	1.131		C(6)	-	H(8)	1.103			
C(1)	-	O(1)	- C(6)	105.7 (5)	C(2)	-	C(3)	- H(5)	115.7		
C(2)	-	O(2)	- C(6)	102.4 (5)	C(4)	-	C(3)	- H(5)	116.7		
C(3)	-	O(3)	- C(4)	60.4 (4)	O(3)	-	C(4)	- C(3)	60.8	(4)	
C(5)	-	O(4)	- H(1)	109.0 (4)	O(3)	-	C(4)	- C(5)	114.8	(5)	
O(1)	-	C(1)	- C(2)	103.9 (5)	O(3)	-	C(4)	- H(6)	114.4		
O(1)	-	C(1)	- H(2)	110.4	C(3)	-	C(4)	- C(5)	118.1	(6)	
O(1)	-	C(1)	- H(3)	105.4	C(3)	-	C(4)	- H(6)	114.3		
C(2)	-	C(1)	- H(2)	119.3	C(5)	-	C(4)	- H(6)	120.3		
C(2)	-	C(1)	- H(3)	114.3	O(4)	-	C(5)	- C(4)	113.2	(6)	
H(2)	-	C(1)	- H(3)	102.9	O(4)	-	C(5)	- C(6)	112.8	(6)	
O(2)	-	C(2)	- C(1)	100.7 (5)	O(4)	-	C(5)	- H(7)	107.5		
O(2)	-	C(2)	- C(3)	108.9 (5)	C(4)	-	C(5)	- C(6)	112.1	(5)	
O(2)	-	C(2)	- H(4)	120.1	C(4)	-	C(5)	- H(7)	104.6		
C(1)	-	C(2)	- C(3)	112.5 (6)	C(6)	-	C(5)	- H(7)	105.9		
C(1)	-	C(2)	- H(4)	118.8	O(1)	-	C(6)	- O(2)	106.4	(5)	
C(3)	-	C(2)	- H(4)	95.9	O(1)	-	C(6)	- C(5)	109.0	(5)	
O(3)	-	C(3)	- C(2)	116.3 (7)	O(1)	-	C(6)	- H(8)	115.6		
O(3)	-	C(3)	- C(4)	58.8 (5)	O(2)	-	C(6)	- C(5)	110.8	(6)	
O(3)	-	C(3)	- H(5)	120.5	O(2)	-	C(6)	- H(8)	106.1		
C(2)	-	C(3)	- C(4)	116.7 (5)	C(5)	-	C(6)	- H(8)	108.9		

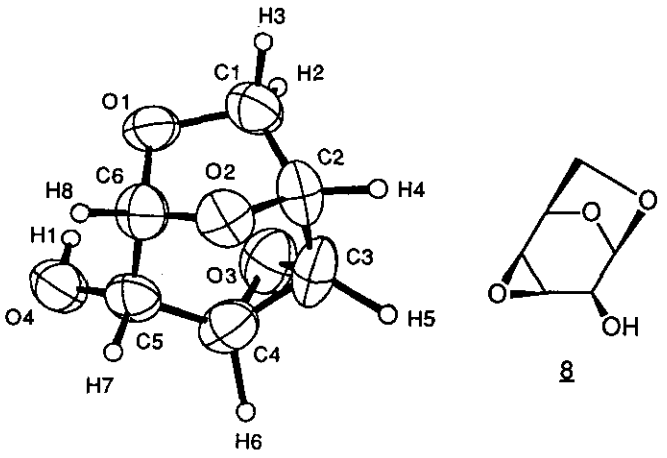
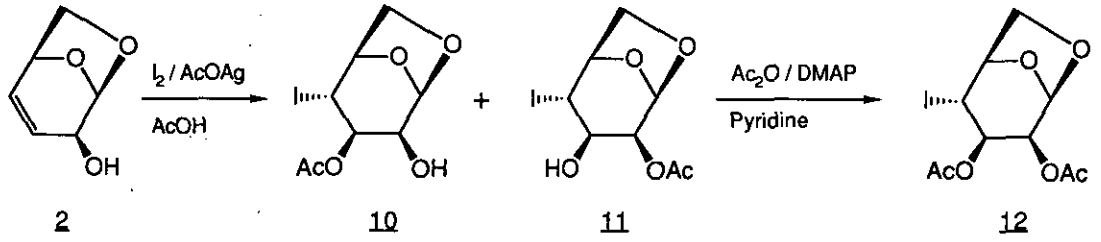


Figure 1 Crystalline structure of 1,6:3,4-dianhydro-β-D-talopyranose (**8**)

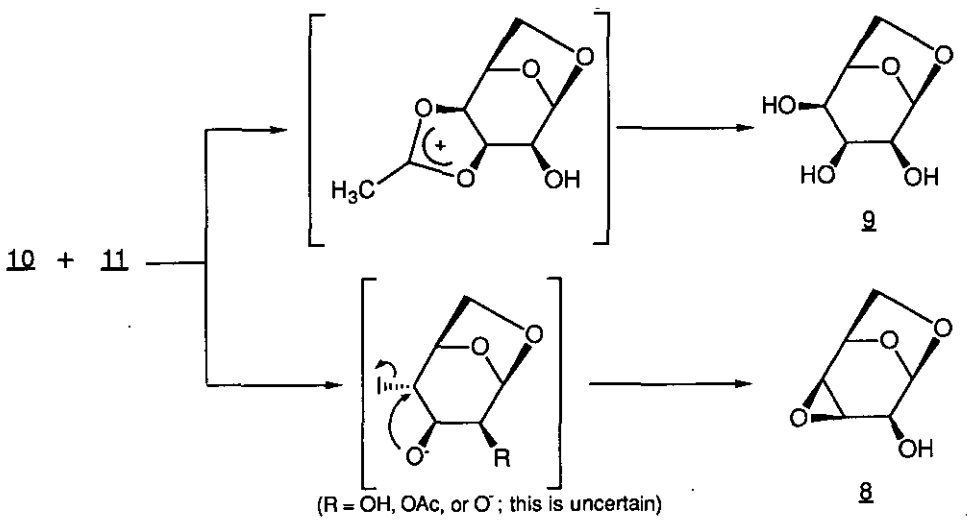
This unexpected result was examined further. Under typical "dry" Prévost conditions (with iodine, silver acetate, and acetic acid), olefin is converted into the iodoacetate *via* an iodonium species. The isolation of the iodoacetate intermediate was attempted (Scheme 3). Treatment of **2** under "dry" Prévost conditions afforded the mixture of two products, each of which had one iodo group, one acetoxyl group, and one hydroxyl group. The mixture could not be separated by column chromatography. Since the acetylation of the mixture afforded iododiacetate (**12**) as a single product, two components of the mixture were determined, **10** and **11** (97.1% yield). Their ^{1}H-nmr spectra and the result of Beilstein testing were within normally expected ranges.



Scheme 3

We assume that the steric hinderance between the 1,6-anhydro- and 3-*O*-acetyl-groups made it difficult to form the acetoxonium ion intermediate on heating of the intermediates (**10**) and (**11**) under "wet" Prévost-Woodward conditions (with water added to the reaction mixture *in situ*.). The alkoxide formed by the following treatment

with ammonia thus attacked the carbon in the 4-position with elimination of the iodide to give epoxide **8** (Scheme 4).[6]



Scheme 4

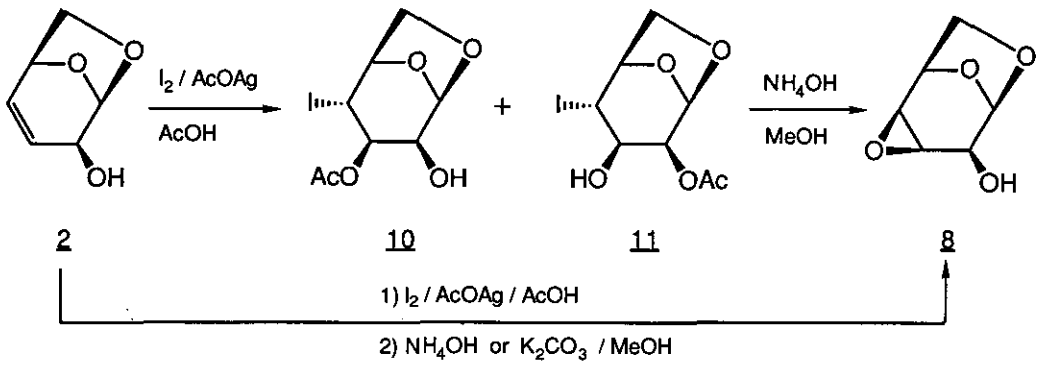
Selective Synthesis of 1,6:3,4-Dianhydro-β-D-talopyranose (**8**); Epoxidation of **2** *via trans*-Iodoacetate.

Epoxide (**8**) is useful as a starting material for syntheses of saccharides. The use of **8** has been described in previous papers.[7] However, previous reports afford **8** from vegetable ivory in low overall yield.[8] Therefore, we attempted to synthesize **8** from **1** stereoselectively and easily in less steps and to give higher yield. On the basis of findings described in the above sections, it was thought that basic-hydrolysis of the intermediate (**10**) and (**11**) would form alkoxide at the 3-position to attack the carbon on the 4-position and eliminate the iodide. The treatment of the mixture of **10** and **11** with ammonia in methanol afforded **8** as a single product with a yield of 97.0% (Scheme 5). The conversions from **2** to **8** were performed in one pot without the isolation of **10** and **11**.

As an alternative condition, the epoxidation of allylic alcohol (**2**) under similar conditions to iodolactonization[9] was attempted. **2** was treated with acetic acid (instead of a carboxylate as used in iodolactonization) and iodine in acetonitrile, followed by hydrolysis with ammonia in methanol to afford **8** in a 31.9% yield. The yield of **8** using this method was lower than that under the conditions of the *trans*-iodoacetoxylation above.

The epoxidation of **2** with *m*-chloroperbenzoic acid in dichloromethane afforded **8** and its diastereomer 1,6:3,4-dianhydro-β-D-altropyranose in yields of 22.9% and 40.3%, respectively. Sharpless oxidation[10] of **2** with

vanadyl acetylacetonate and *tert*-butyl hydroperoxide in toluene afforded **8** and 1,6:3,4-dianhydro-β-D-altropyranose in very low yields.



Scheme 5

It was also noted that the present epoxidation *via trans*-iodoacetate intermediate with iodine and silver acetate resulted in stereoselective formation of an oxiran ring on a sterically hindered site of the C-C double bond of **8**. This method is expected to be applicable to various olefins.

CONCLUSIONS

An easy method for preparing 1,6:3,4-dianhydro-β-D-talopyranose (**8**) from levoglucosenone (**1**) *via trans*-iodoacetate intermediate was developed. The structure of **8** is suitable as a starting material for syntheses of various saccarides. It is noted that epoxidation *via trans*-iodoacetoxylation with iodine and silver acetate stereoselectively forms an oxiran ring on a sterically hindered site of the C-C double bond of **8** , and this method is expected to be applicable to various olefins.

EXPERIMENTAL

Spectral Measurements.

All 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.

1,6-Anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**).[2,3e,3f,11]

A solution of 7.98 g (63.3 mmol) of levoglucosenone (**1**) in 130 ml of dry ether was added dropwise to 2.42 g (63.8 mmol) of lithium aluminium hydride in 200 ml of dry ether cooled with ice, and was stirred for 1 h at room temperature. Lithium aluminium hydride was then decomposed by careful addition of 4.6 ml of water. The mixture was diluted with methanol, filtered through a Celite pad, and the residue was washed with methanol. The filtrate was evaporated under reduced pressure (<40°C) to give a yellow oil. The oil was separated by column chromatography on silica gel (eluent: hexane / ether = 1/1;v/v). The first fraction was evaporated under reduced pressure, and recrystallization of the product from hexane-ether afforded 5.70 g (70.3%) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) as white needles. mp 65.6-66.4°C; $[\alpha]^{25}_D$ -30.3° (*c* 1.00, $CHCl_3$) (lit.,[12] mp 65-66.5°C; $[\alpha]_D$ -35.3°, *c* 1, $CHCl_3$); ir (KBr) 3412 (br), 3050 (w), 1487 (w), 1425 (m), 1354 (m), 1259 (w), 1180 (m), 1125 (s), 1071 (s), 1046 (s), 965(s), 919 (m), 884 (m), 861 (m), 820 (s), 731 (m), 681 (w), 648 (w), and 576 cm^{-1} (m); ^{1}H-nmr ($CDCl_3$) δ 6.12 (1H, dd, *J*=9.9 and 4.2 Hz, H-4), 5.72 (1H, ddd, *J*=9.9, 2.9, and 2.2 Hz, H-3), 5.52 (1H, br, H-1), 4.67 (1H, dd, *J*=4.2 and 4.1 Hz, H-5), 4.34 (1H, m, H-2), 3.84 (1H, d, *J*=6.6 Hz, H-6'), 3.78-3.74 (1H, dd, *J*=6.6 and 4.1 Hz, H-6), 2.10 (1H, d, *J*=12.0 Hz, OH). Anal. Calcd for $C_6H_8O_3$: C,56.25; H,6.29. Found: C,56.08; H,6.33.

Prévost-Woodward reaction upon 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) under "wet" conditions (followed by the basic-hydrolysis).

To a stirred and mixed solution of 128 mg (1.00 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) and 334 mg (2.00 mmol) of silver acetate in 4.6 ml of acetic acid was slowly added 267 mg (1.05 mmol) of iodine at room temperature. The mixture was stirred for 5 h at room temperature under a nitrogen atmosphere. To the reaction mixture was added 0.45 ml of acetic acid containing 4% water. The mixture was vigorously stirred for 4 h at 90-95 °C. After cooling, 260 mg of sodium chloride was added to the reaction mixture The mixture was slowly poured into an ice-cooled aqueous sodium hydrogen carbonate solution (7.7 g of sodium hydrogen carbonate in 100 ml of water). The mixture was filtered off and washed with methanol and water. The filtrate was evaporated under reduced pressure. To the residue was added 10 ml of 25% ammonia and 50 ml of methanol, followed by stirring for 13 h at room temperature. The mixture was evaporated under reduced pressure. Two products from the residue were separated by column chromatography on silica gel . The first fraction (eluent: n-hexane / ethyl acetate = 1/1; v/v) gave 89 mg (62%) of 1,6:3,4-

dianhydro-β-D-talopyranose (**8**), and the second (eluent: chloroform / acetone = 1/4; v/v), 29 mg (18%) of 1.6-anhydro-β-D-talopyranose (**9**). **8** was recrystallized from *n*-hexane-ether (1:4; v/v).

1,6:3,4-Dianhydro-β-D-talopyranose (**8**); mp 74.0-75.2°C; $[\alpha]^{24}_D$ -49.7° (*c* 1.44, H_2O) (lit.,[8b] mp 73-74°C; $[\alpha]_D$ -49.5°, *c* 1.44, H_2O); ir (KBr) 3440 (br), 1427 (w), 1408 (w), 1346 (w), 1309 (w), 1259 (w), 1149 (m), 1096 (w), 1065 (s), 1025 (w), 998 (m), 975 (s), 917 (s), 870 (w), 843 (w), 816 (m), 754 (w), 698 (m), 621 (m), 588 (br), 516 (m), 474 (m), 451 (w), and 416 cm^{-1} (m); ^{1}H-nmr ($CDCl_3$) δ 5.30 (1H, d, *J*=3.8 Hz, H-1), 4.82 (1H, dd, *J*=4.7 and 4.7 Hz, H-5), 3.95 (1H, d, *J*=6.6 Hz, H-6), 3.83-3.76 (2H, m, H-2 and H-4), 3.56 (1H, dd, *J*=6.6 and 4.7 Hz, H-6'), 3.34 (1H, ddd, *J*=3.9, 3.9, and 1.0 Hz, H-3), 2.41 (1H, d, *J*=12.2 Hz, OH); ^{13}C-nmr ($CDCl_3$) δ 98.2 (C-1), 72.1 (C-5), 68.9 (C-2), 64.3 (C-6), 57.6 (C-4), 50.6 (C-3). Anal. Calcd for $C_6H_8O_4$: C,50.00; H,5.60. Found: C,49.98; H,5.64.

1,6-Anhydro-β-D-talopyranose (**9**);[5] ^{1}H-nmr (D_2O) δ 5.15 (1H, br, H-1), 4.26 (1H, dd, *J*=4.7 and 4.7 Hz, H-5), 4.18 (1H, d, *J*=7.7 Hz, H-6), 3.96 (1H, dddd, *J*=4.7, 4.7, 1.1, and 1.1 Hz, H-4), 3.79-3.74 (1H, m, H-3), 3.52-3.46 (2H, m, H-2 and H-6').

trans-Iodoacetoxylation upon 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**).

a) *trans*-Iodoacetoxylation: To a stirred and mixed solution of 128 mg (1.00 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) and 334 mg (2.00 mmol) of silver acetate in 4.6 ml of acetic acid was slowly added 267 mg (1.05 mmol) of iodine at room temperature. The mixture was stirred for 5 h at room temperature under a nitrogen atmosphere. 200 mg of sodium iodide was added to the reaction mixture, and then the mixture was poured into aqueous sodium hydrogen carbonate solution (7.10 g of sodium hydrogen carbonate in 100 ml of water). The precipitate was filtered off and washed with methanol and water. The filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 1/1; v/v) to afford 305 mg (97.1%) of the mixture of 3-*O*-acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**10**) and 2-*O*-acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**11**) as a colorless oil. The ratio of **10** : **11** was 57 : 43, determined by ^{1}H-nmr spectral analysis of the mixture.

3-*O*-Acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**10**); ^{1}H-nmr ($CDCl_3$) δ 5.45 (1H, br, H-1), 5.35 (1H, ddd, *J*=5.5, 2.7, and 1.3 Hz, H-3), 4.63 (1H, d, *J*=5.5 Hz, H-5), 4.27 (1H, br, H-4), 4.20 (1H,

ddd, *J*=11.6, 5.5 and 1.9 Hz, H-2), 4.11 (1H, dd, *J*=7.9, and 0.7 Hz, H-6), 3.82-3.76 (1H, m, H-6), 2.39 (1H, d, *J*=11.6 Hz, OH), 2.16 (3H, s, OAc).

2-*O*-Acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**11**); ^{1}H-nmr ($CDCl_3$) δ 5.53 (1H, br, H-1), 5.20 (1H, dd, *J*=4.8, and 1.6 Hz, H-2), 4.72 (1H, d, *J*=4.8 Hz, H-5), 4.48 (1H, ddd,*J*=5.0, 5.0, and 1.6 Hz, H-3), 4.41-4.39 (2H, m, H-4 and H-6), 3.82-3.76 (1H, m, H-6'), 3.23 (1H, d, *J*=5.3 Hz, OH), 2.18 (3H, s, OAc).

b) Acetylation of **10** and **11**: 2,3-*O*-diacetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**12**): A solution containing 314 mg of the mixture of 3-*O*-acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**10**) and 2-*O*-acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**11**), 0.19 ml of acetic anhydrate, 0.32 ml of pyridine, and a catalytic 4-dimethylaminopyridine in 10 ml of dichloromethane was stirred for 4 h at room temperature under a nitrogen atmosphere. The reaction mixture was poured into 100 ml of the ice-cooled saturated sodium hydrogen carbonate solution, and extracted with dichloromethane three times. The organic layer was washed with saturated copper(II) sulfate solution (twice), followed with water (twice), and then was dried over anhydrous magnesium sulfate. The solvent was distilled off under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 1/1; v/v) to afford 313 mg (87.9%) of 2,3-*O*-diacetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**12**). This was recrystallized from *n*-hexane-ether-dichloromethane. mp 95.5-96.1°C; $[\alpha]^{26}_D$ -187.2° (*c* 1.03, $CHCl_3$); ir (KBr) 1750 (s), 1373 (m), 1236 (s), 1143 (m), 1110 (w), 1069 (s), 982 (m), 897 (m), 837 (w), 721 (w), 687 (w), 663 (w), 615 (w), 592 (w), 522 (w), and 460 cm^{-1} (w); ^{1}H-nmr ($CDCl_3$) δ 5.53 (1H, dd, *J*=5.1 and 1.4 Hz, H-3), 5.49 (1H, br, H-1), 5.36 (1H, dd, *J*=5.1 and 1.6 Hz, H-2), 4.69 (1H, dd, *J*=5.4 and 0.6 Hz, H-5), 4.29 (1H, dd, *J*=7.8and 0.6 Hz, H-6), 4.25 (1H, br, H-4), 3.84 (1H, dd, *J*=7.8 and 5.4 Hz, H-6'), 2.15 (3H, s, OAc), 2.08 (3H, s, OAc'); ^{13}C-nmr ($CDCl_3$) δ 170.0 (C=O), 169.8 (C=O), 100.2 (C-1), 78.1 (C-5), 73.1 (C-3), 68.5 (C-6), 66.0 (C-2), 23.9 (C-4), 21.2 (CH_3), 21.0 (CH_3). Anal. Calcd for $C_{10}H_{13}O_6I$: C,33.73; H,3.68; I,35.64. Found: C,33.67; H,3.56; I,35.29.

1,6:3,4-Dianhydro-β-D-talopyranose (**8**).

Method using iodine and silver acetate in acetic acid.

a) From the mixture **10** and **11**: A solution containing 361 mg of the mixture of 3-*O*-acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-hexopyranose (**10**) and 2-*O*-acetyl-1,6-anhydro-4-deoxy-4-iodo-β-D-*lyxo*-

hexopyranose (**11**), 192 mg of silver acetate, and 46 ml of 25% ammonia in 46 ml of methanol was stirred at room temperature overnight. The precipitate was filtered off and washed with water, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 1/1; v/v) to afford 161 mg (97.0%) of 1,6:3,4-dianhydro-β-D-talopyranose (**8**).

b-1) From allylic alcohol **2** directly (the basic condition with ammonia water); To a stirred and mixed solution of 128 mg (1.00 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) and 334 mg (2.00 mmol) of silver acetate in 4.6 ml of acetic acid was slowly added 267 mg (1.05 mmol) of iodine at room temperature. The mixture was stirred for 5 h at room temperature under a nitrogen atmosphere (until the iodine was consumed completely), whereupon 40 ml of 25% ammonia and 40 ml of methanol were added to the reaction mixture, followed by stirring at room temperature overnight. The precipitate was filtered off and washed with water, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 1/1-3; v/v) to afford 135 mg (93.8%) of 1,6:3,4-dianhydro-β-D-talopyranose (**8**).

b-2) From allylic alcohol **2** directly (the basic condition with potassium carbonate); To a stirred and mixed solution of 128 mg (1.00 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) and 334 mg (2.00 mmol) of silver acetate in 4.6 ml of acetic acid was slowly added 267 mg (1.05 mmol) of iodine at room temperature. The mixture was stirred for 5 h at room temperature under a nitrogen atmosphere (until the iodine was consumed completely), whereupon 7.70 g (55.7 mmol) of potassium carbonate and 7.10 g (84.5 mmol) of sodium hydrogen carbonate in 150 ml of methanol and 10 ml of water were slowly added to the reaction mixture with ice-cooling, followed by stirring for 2 days at room temperature. The precipitate was filtered off and washed with water, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 1/1-3; v/v) to afford 109 mg (75.6%) of 1,6:3,4-dianhydro-β-D-talopyranose (**8**).

Method using iodine and acetic acid in acetonitrile.

To a stirred and mixed solution of 128 mg (1.00 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) and 1.82 ml (31.8 mmol) of acetic acid in 7.0 ml of acetonitrile was slowly added 1.32 g (5.18 mmol) of iodine at room temperature. The mixture was stirred for 29 h at 40 °C under a nitrogen atmosphere (untill the iodine was consumed completely), whereupon 20 ml of 25% ammonia and 20 ml of methanol were added to the reaction mixture, followed by stirring at room temperature overnight. The precipitate was filtered off and washed with water, and the filtrate was evaporated under reduced pressure. The residue was purified

by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 1/1-3; v/v) to afford 46 mg (31.9%) of 1,6:3,4-dianhydro-β-D-talopyranose (**8**).

Oxidation of allylic alcohol **2** with peroxides.

a) Oxidation of allylic alcohol **2** with *m*-chloroperbenzoic acid.

To a solution of 256 mg (2.00 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) in 4 ml of dry dichloromethane was added a mixture of 1.38 g (5.60 mmol) of 70% *m*-chloroperbenzoic acid and 8 ml of dry dichloromethane stepwise at room temperature, which was stirred for 3 days at room temperature. The precipitate was filtered off and washed with dichloromethane. To the filtrate was added a solution of 1.00 g (7.93 mmol) of sodium sulfite and 840 mg (10.0 mmol) of sodium hydrogen carbonate in water, which was stirred for 5 min. The mixture was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 1/1-3; v/v) to separate the two products. The first fraction gave 66 mg (22.9%) of 1,6:3,4-dianhydro-β-D-talopyranose (**8**), and the second fraction gave 116 mg (63.2%) of 1,6:3,4-dianhydro-β-D-altropyranose.

1,6:3,4-Dianhydro-β-D-altropyranose was recrystallized from *n*-hexane-ethyl acetate-ether. mp 161.0-161.8°C; $[\alpha]^{25}_{D}$ -116.6° (*c* 0.53, H_2O) (lit.,[13] mp 161-162°C; $[\alpha]^{18}_{D}$ -121°, *c* 0.53, H_2O); ir (KBr) 3396 (br), 1419 (m), 1359 (w), 1238 (m), 1191 (w), 1141 (m), 1089 (s), 1060 (m), 1009 (w), 977 (m), 949 (m), 878 (m), 853 (w), 810 (m), 698 (m), 634 (w), 592 (w), 532 (w), and 470 cm^{-1} (m); ^{1}H-nmr ($CDCl_3$) δ 5.33 (1H, dd, *J*=2.9 and 2.8 Hz, H-1), 4.74 (1H, d, *J*=4.5 Hz, H-5), 4.06 (1H, d, *J*=7.5 Hz, H-6), 3.88 (1H, dd, *J*=7.5 and 4.5 Hz, H-6'), 3.85 (1H, dd, *J*=11.5 and 2.9 Hz, H-2), 3.14 (1H, d, *J*=3.5 Hz, H-4), 3.01 (1H, dd, *J*=3.5 and 2.8 Hz, H-3), 2.26 (1H, d, *J*=11.5 Hz, OH). Anal. Calcd for $C_6H_8O_4$: C,50.00; H,5.60. Found: C,49.79; H,5.56.

b) Sharpless oxidation of allylic alcohol **2**.[10]

A solution of 256 mg (2.00 mmol) of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**) in 2 ml of dry toluene was added to a mixture of 13 mg (0.05 mmol) of vanadyl acetylacetonate in 2 ml of dry toluene under a nitrogen atomosphere, and then a solution of 1.92 ml of *tert*-butyl hydroperoxide, 2.5 $mol \cdot dm^{-3}$ solution in dry toluene, was added dropwise to the reaction mixture. The reaction mixture was stirred for 24 h at 40°C, followed by stirring for 46 h at 80°C under a nitrogen atomosphere. After cooling to room temperature, 605 mg (4.80 mmol) of sodium sulfite was added to the reaction mixture, which was then stirred for 5 min.

The precipitate was filtered off and washed with toluene. The filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: *n*-hexane / ethyl acetate = 1/1-3; v/v) to separate the two products. The first fraction gave 26 mg (9.0%) of 1,6:3,4-dianhydro-β-D-talopyranose (**8**), and the second fraction gave, 15 mg (5.2%) of 1,6:3,4-dianhydro-β-D-altropyranose.

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