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**CATALYTIC, STEREOSELECTIVE GLYCOSYLATION -
SPIROKETALIZATION OF 3,4,5-TRI-*O*-BENZYL- β -D-
FRUCTOPYRANOSE GENERATING DI-D-FRUCTO-
PYRANOSE-1,2':2,1'-DIANHYDRIDE**

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Abstract – α -D-Fructopyranose β -D-fructopyranose-1,2':2,1'- dianhydride has been stereoselectively synthesized by tandem catalytic glycosylation-spiroketalization of 3,4,5-tri-*O*-benzyl- β -D-fructo- pyranose. Of the several protic acid catalysts which exist, 0.3 molar equivalent trifluoromethane sulfonic acid in toluene was found to be most effective to afford the dianhydride in good yield.

Di- D-fructose dianhydrides (DFAs) are well known sugar-based spiroketals possessing three ring systems comprising two D-fructose moieties attached to the central 1,4-dioxane ring.¹ According to the sugar ring sizes and the anomeric stereochemistry, DFAs are divided into five types as Type I – V along with thirteen isomers (Figure 1).^{1,2} Some members of DFAs have been isolated from microorganisms³ and higher plants,⁴ however only generally as complex mixture of isomeric compounds. They have been anticipated as being potential food materials for use as sweeteners⁵ and bifidogenic agents,⁶ as well as metal cation complexing promoters.⁷ They might also be utilized as chiral templates for molecular recognition.⁸

Aiming at chemical synthesis of DFAs, promotion by thermolysis⁹ or protonation¹⁰ with anhydrous hydrogen fluoride of D-fructose, sucrose, and inulin combined to form DFAs in high yield. Meanwhile, the proportion of each product in the mixture would depend on the reaction conditions employed. A concise, stereo-controlled synthesis of DFAs has been developed² by tandem acetal cleavage, intermolecular glycosylation, and intramolecular spiroketalization of protected 1,2-*O*-isopropylidene- β -D-fructofuranose or -pyranose, where protic or Lewis acid-promoted reactions

were employed to give α,α -dianhydride and α,β -dianhydride of di-D-fructofuranose (Type I) as well as di-D-fructopyranose (Type III).

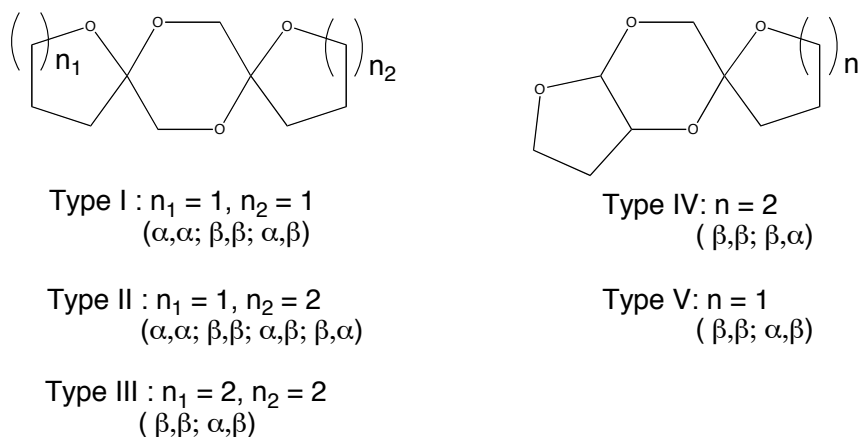


Figure 1 Various kinds of di-D-fructose dianhydrides (DFAs)

The proportion of the isomers could be controlled by the judicious choice of protecting groups, i.e. non-participating groups such as benzyl or allyl group prefer non-symmetric structures (α,β -DFAs), whilst participating groups such as benzoyl favor C_2 -symmetric structure (α,α - or β,β -DFAs) in good diastereoselectivity. The only disadvantage of employing this method is that it requires an excessive use (1.5 - 2.0 equivalent) of acids for one-pot, tandem reactions.

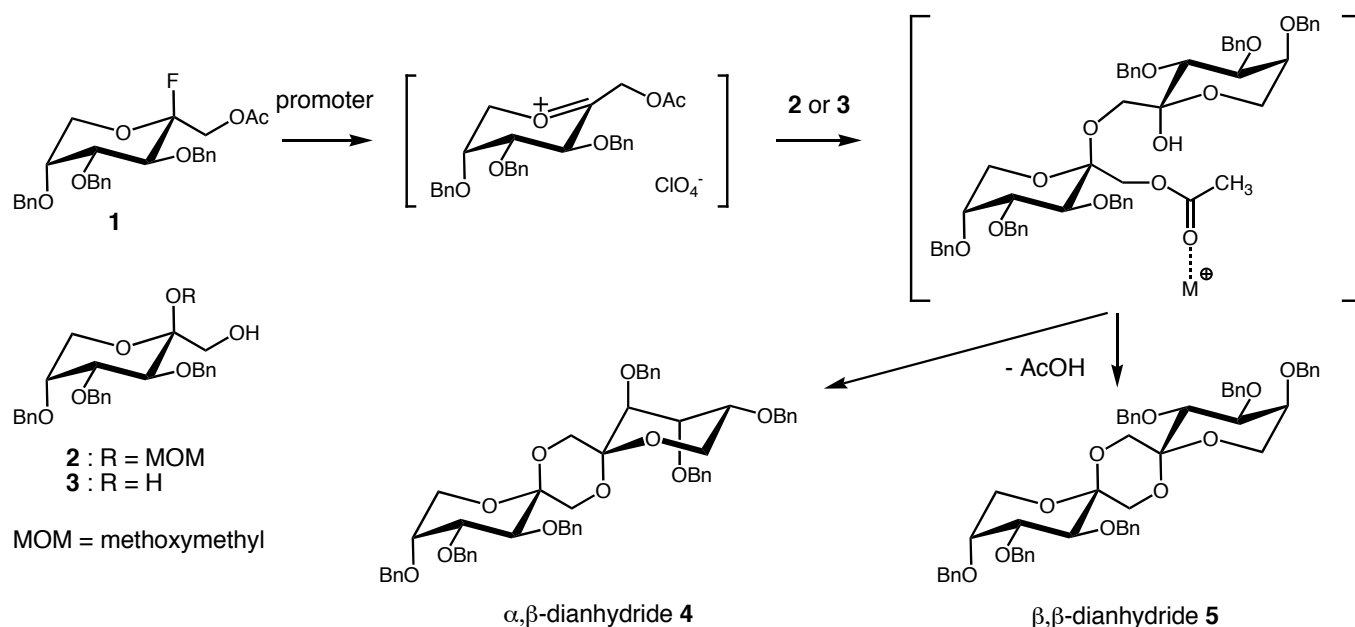
We herein propose an alternative method, i.e., an environmentally benign synthesis of α -D-fructopyranose β -D-fructopyranose-1,2':2,1'-dianhydride (**4**),^{1,2} a Type III DFA, by catalytic, stereoselective glycosylation-spiroketalization of 3,4,5-tri-*O*-benzyl- β -D-fructopyranose (**3**) in 80% yield.

Results and discussion : In our continuous study on chemical synthesis of fructooligosaccharides aiming at creating new frameworks, we recently reported the isolation of a Type III DFA as a byproduct of β -D-fructopyranosyl-(2 $\rightarrow$ 1)- β -D-fructopyranoside in low yield.¹² According to this outcome, we attempted to obtain D-fructopyranose-1,2':2,1'-dianhydride (**4**) by stereo- and chemoselectively using 1-*O*-acetyl-3,4,5-tri-*O*-benzyl- β -D-fructopyranosyl fluoride (**1**)¹² as the reactive glycosyl donor and 3,4,5-tri-*O*-benzyl- β -D-fructopyranose (**3**) as the acceptor.¹² Of the several promoters available used for activation of glycosyl fluoride, $\text{SnCl}_2\text{-AgClO}_4$,¹³ $\text{Cp}_2\text{HfCl}_2\text{-AgClO}_4$,¹⁴ and $\text{Cp}_2\text{HfCl}_2\text{-AgOTf}$ ¹⁵ resulted in the formation of DFAs as is summarized in Scheme 1 and Table 1.

Table 1. Synthesis of Di-D-Fructopyranose-1,2':2,1'-dianhydride Using Fructosyl Fluoride as the Glycosyl Donor ^a

Run	Donor	Acceptor	A/D ^{b)}	Promotor (equiv.) ^{c)}	Time (h)	Yield of 4 (%)
1	1	2	1.2	SnCl ₂ -AgClO ₄ (2 – 2)	3	57
2	1	3	1.2	SnCl ₂ -AgClO ₄ (2 – 2)	120	52
3	1	3	1.2	Cp ₂ ZrCl ₂ -AgClO ₄ (1 – 1)	120	—
4	1	3	2.0	Cp ₂ HfCl ₂ -AgClO ₄ (5 – 5)	5	quant.
5	1	3	2.0	Cp ₂ HfCl ₂ -AgOTf (5 – 5)	5	25
6	—	3	—	Cp ₂ HfCl ₂ -AgClO ₄ (5 – 5)	5	46

a) All reactions were performed in dichloromethane. b) Ratio of the molar equivalent employed. c) Molar equivalent to the donor employed.

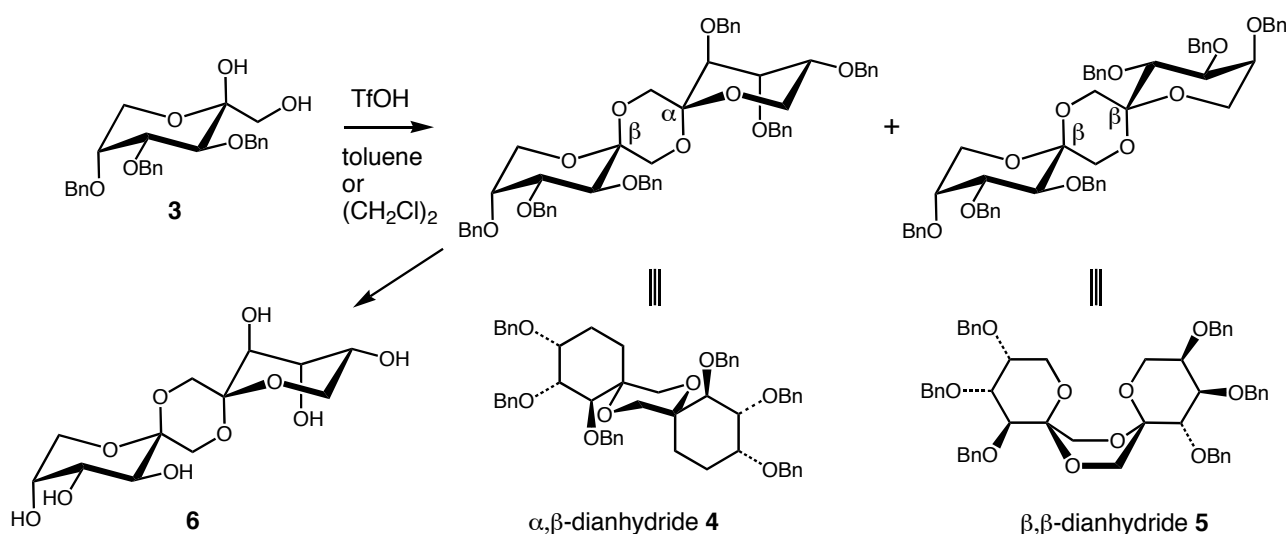


Scheme 1 Postulated reaction mechanism generating di-D-fructose dianhydrides (**4** and **5**)

When the fructosyl fluoride was reacted with 2-*O*-methoxymethyl 3,4,5-tri-*O*-benzyl-β-D-fructopyranoside¹² in the presence of SnCl₂-AgClO₄ in dichloromethane, α-D-fructopyranose β-D-fructopyranose-1,2':2,1'-dianhydride (**4**) was obtained in 57% yield (Run 1). This compound might be formed by way of β-D-fructopyranosyl-(2→1)-β-D-fructopyranoside, which gave dianhydride (**4**) through the de-*O*-MOM reaction with strong Lewis acidic stannous chloride promoter followed by intramolecular cyclization (Scheme 1). Accordingly, direct use of 3,4,5-tri-*O*-benzyl-β-D-fructopyranose (**3**) as the acceptor would conceivably afford DFA (**4**) without the de-*O*-MOM reaction. In fact, an analogous procedure employing hydroxyl-free acceptor (**3**) gave DFA

(4) in 52% yield (Run 2). Of the alternative Lewis acid promoters tested, such as zirconocen or hafnocen tested, excess use of $\text{Cp}_2\text{HfCl}_2\text{-AgClO}_4$ system resulted in the best yield (Run 4).

The reaction mechanism could be postulated through an oxocarbenium intermediate, which glycosylate the acceptor (3) followed by spiroketalization along with the conformational change and with the elimination of acetic acid to give the dianhydride (4), as is depicted in Scheme 1. An analogous mechanism has been proposed¹⁶ for spiroketalization generating spiro-ketodisaccharide via oxocarbenium intermediate starting from 3,4,5,7-tetra-*O*-benzyl- α -D-hept-2-ulopyranoses.



Scheme 2 Chair and boat conformation of di-D-fructose dianhydrides (4 and 5)

Although the above-described access to DFAs using a fluoride donor resulted in a high yield of 4, preparation of 1 as well as excess use of promoters are cumbersome. It should be noted that the acceptor itself dimerized to DFA (4) under similar reaction conditions in the absence of the fluoride donor (1) (Table 1, Run 6). We anticipated accordingly an alternative route to 4, such that the above acceptor would dimerize to DFA (4) via a self-condensation reaction under appropriate acidic conditions. In fact, fructopyranose (3) was exposed to several kinds of acid to afford per-*O*-benzylated di-D-fructopyranose-1,2':2,1'-dianhydride (4) as shown in Table 2.

The use of catalytic amount of *p*-toluenesulfonic acid, camphorsulfonic acid, and triflic acid in refluxed toluene resulted in low yields (Run 1-3). Subsequently, the use of a catalytic amount (0.3 eq.) of triflic acid in toluene or 1,2-dichloroethane at an ambient temperature resulted in the formation of the expected dianhydride (4) in 86-88% yield (Run 4-5). In a large scale experiment a byproduct was isolated in 8% yield, which was characterized to be di- β -D-fructopyranose-1,2':2,1'-dianhydride (5).^{1,2}

Structural analyses of α,β -dianhydride (**4**) and β,β -dianhydride (**5**) were reasonably elucidated on the basis of their NMR spectra, comparing with those of the reported data.^{1,2}

Table 2. Synthesis of Di-D-Fructopyranose-1,2':2,1'-dianhydride by Self-condensation of 3,4,5-tri-*O*-benzyl- β -D-fructopyranose

Run	Promotor	(equiv.) ^{a)}	Solvent	Temp. (°C)	Time (h)	Yield of 4 (%)
1	TsOH	(0.1)	Toluene	130	2	29
2	CSA	(0.1)	Toluene	130	1	16
3	TfOH	(0.1)	Toluene	130	2	—
4	TfOH	(0.3)	Toluene	r.t.	0.5	88
5	TfOH	(0.3)	(CH ₂ Cl) ₂	r.t.	0.5	86
6	TfOH	(0.6)	THF	r.t.	1	71

a) Molar equivalent to the fructopyranose employed.

As indicated in Fernandez's report, in Type III DFAs, the major conformer should be favored with relative stability of the incipient 1,4-dioxane ring. In the α,β -isomer (**4**), 1,4-dioxane ring takes chair form, and the α - and β -D-fructopyranose rings adopt the 4C_1 and 1C_4 chair conformation, respectively, which are reasonably supported by their H^1 -NMR coupling constants, i.e. $J_{3,4} = 4.0$, $J_{4,5} = 3.5$, $J_{5,6a} = 5.0$, and $J_{5,6b} = 9.0$ Hz for 4C_1 conformation of the α -anomeric residue, whilst $J_{3',4'} = 10.0$, $J_{4',5'} = 4.0$, $J_{5',6'a} = 2.0$, and $J_{5',6'b} = 1.0$ Hz for 1C_4 conformation of the β -anomeric residue. At this conformation both oxygen-substituents (each pyranose oxygen atom) fit the anomeric effect so that they take on an axial disposition to the 1,4-dioxane ring, while the carbon substituents (C1-carbon of the fructose moieties) are oriented to an equatorial disposition. Conversely, for the β,β -isomer central 1,4-dioxane ring should take on a less stable boat conformation in order to accommodate the anomeric effect at both anomeric centers (Scheme 2). In this case, the third-order structure of the molecule might be consistent with C_2 -symmetric form, which simplify the NMR spectral data just like a monosaccharide (cf. Experimental). The boat arrangement of the 1,4-dioxane ring of the β,β -isomer was reported even in crystalline form on the basis of its X-Ray crystallographic data.¹⁷

α,β -Predominant stereoselectivity on the spiroketalization over β,β -isomer would be rationalized in terms of thermodynamic control, by which chair-chair-chair arrangement of the three rings of α,β -isomer predominates the chair-boat-chair form of the α,β -isomer.^{1,2}

Then, the major α,β -isomer was subjected to de-*O*-benzylation by catalytic hydrogenation with Pd-C/H₂ in AcOH-MeOH-H₂O medium to give hydroxyl free α -D-fructopyranose β -D-fructopyranose-1,2':2,1'-dianhydride (**6**)¹ in quantitative yield.

In summary, we have developed a new route to α -D-fructopyranose β -D-fructopyranose-1,2':2,1'-dianhydride by tandem glycosylation-spiroketalization reaction of 3,4,6-tri-*O*-benzyl- β -D-fructopyranose with fructosyl fluoride, and then self condensation of **3** using TfOH (0.3 eq.) in toluene or 1,2-dichloroethane to afford dianhydride in 80% yield. The only byproduct is found to be the β,β -isomer, of which the yield was estimated at less than 8%. Application of this method to other types of di-D-fructose dianhydrides using catalytic spiroketalization is in progress.

EXPERIMENTAL

Melting points were determined on a Yamato MP-1 apparatus and are uncorrected. Spectral data were recorded on the following instruments; Jasco P-1080 ($[\alpha]_D$), JMS-AX 505 H (MS), and Varian XL-400 and VXR-300 (NMR in chloroform-*d* solution). Column chromatography was carried out on silica gel (Kanto Kagaku Co.: up to 100 mesh) column. TLC was achieved on silica gel 60 F254 (Merck Art. 5735). The spots were detected by UV light (254 nm) or charring with 10% aq. sulfuric acid. Compounds (**1**, **2**, and **3**) were obtained by the method described in the literature.¹²

Per-*O*-benzyl- α -D-fructopyranose β -D-fructopyranose-1,2':2,1'-dianhydride (**4**)

Method A (Experiment for Table 1, Run 1): To a stirred suspension of **2** (24.7 mg, 0.05 mmol) in dry CH₂Cl₂ (2 mL) with MS-4A (powder, 100 mg) were added SnCl₂ (9.4 mg, 0.05 mmol), AgClO₄ (11.5 mg, 0.05 mmol), and **1** (24.5 mg, 0.05 mmol). The mixture was stirred in the dark at rt for 2.5 h, and then diluted with CH₂Cl₂ (1 mL), filtered through a pad of Celite. The filtrate was washed with 5% aq. NaHCO₃ (10 mL) and water (3 x 10 mL), dried (Na₂SO₄), and evaporated to give the residue, which was eluted from a silica gel column with hexane-AcOEt (10:1→5:1→1:1, gradient). The major fraction was concentrated to afford the dianhydride (**4**) (24.5 mg, 0.02mmol) in 56% yield as a yellowish syrup: $[\alpha]_D^{28}$ -12.0° (c=1.0, CHCl₃) [lit.,¹ -59.0° (c=1.0, CHCl₃)]; MS (FAB) *m/z* : 865 [M+H]⁺, 887 [M+Na]⁺; ¹H-NMR (400MHz, CDCl₃) δ : 3.30 (1H, d, H-1'a), 3.51 (1H, dd, H-6'a), 3.62 (1H, dd, H-6a), 3.69 (1H, dd, H-1a), 3.70 (1H, dd, H-4), 3.71 (1H, d, H-3), 3.74 (1H, d, H-3'), 3.74 (1H, d, H-1b), 3.75 (1H, ddd, H-5'), 3.80 (1H, dd, H-6'b), 3.83 (1H, ddd, H-5), 3.94 (1H, dd, H-6b), 3.99 (1H, dd, H-4'), 4.16 (1H, dd, H-1'b); *J*_{1a,1b} = 11.5, *J*_{3,4} = 3.0, *J*_{4,5} = 3.0, *J*_{5,6a} = 4.0, *J*_{5,6b} = 9.0, *J*_{6a,6b} = 11.0, *J*_{1'a,1'b} = 11.5, *J*_{3',4'} = 9.5, *J*_{4',5'} = 3.0, *J*_{5',6'a} = 1.0, *J*_{5',6'b} = 2.0, *J*_{6'a,6'b} = 12.5 Hz; ¹³C-NMR (100MHz, CDCl₃) δ : 58.93 (C-6), 60.58 (C-6'), 61.12 (C-1), 61.30 (C-1'), 71.28, 71.40, 72.11, 72.36, 73.52, 75.40 (6×Ph-CH₂), 72.28 (C-5), 73.73 (C-3), 73.76 (C-5'), 76.11 (C-3'), 77.59 (C-4), 78.28 (C-4'), 94.56 (C-2'), 95.82 (C-2).

Method B (Experiment for Table 1, Run 2) : 3,4,5-Tri-*O*-benzyl- β -D-fructopyranose (**3**) (27 mg, 0.06 mmol) and the fructosyl fluoride (**1**) (24.5 mg, 0.05 mmol) were employed for SnCl_2 - AgClO_4 -promoted reaction conditions as described for Method A. Aqueous workup and purification through silica gel column chromatography eluting with toluene-AcOEt (1:1) afforded 22.4 mg (52%) of **4** as a yellowish syrup.

Method C (Experiment for Table 1, Run 4) : The acceptor (**3**) (45 mg, 0.1 mmol) and the donor (**1**) (24.7 mg, 0.05 mmol) were dissolved in dry CH_2Cl_2 (2.0 mL) with MS-4A (powder, 100 mg). Hafnocene dichloride Cp_2HfCl_2 (95.3 mg, 0.25 mmol) and AgClO_4 (52.0 mg, 0.25 mmol) were added to the mixture, which was stirred at rt for 5 h. The resulting mixture was worked up as described for Method B to give 43 mg (quantitative) of **4** as a yellowish syrup.

Method D (Experiment for Table 1, Run 6) : To a solution of **3** (45 mg, 0.1 mmol) in dry CH_2Cl_2 (1.0 mL) were added Cp_2HfCl_2 (95.3 mg, 0.25 mmol) and AgClO_4 (52.0 mg, 0.25 mmol), and the mixture was stirred at rt for 5 h. General workup as described above afforded 20 mg (46%) of **4** as a yellowish syrup.

Method E (Promotion by TfOH), a scale up procedure : Trifluoromethanesulfonic acid (29.1 μL , 0.30 mmol) was added to a solution of **3** (500 mg, 1.10 mmol). The mixture was stirred at rt for 0.5 h, and then worked up as described above to yield 380 mg (80%) of **4** as a colorless amorphous powder and 39 mg (8.2%) of the β,β -isomer (**5**) as a colorless amorphous powder.

Per-*O*-benzyl- β -D-fructopyranose β -D-fructopyranose 1,2':2,1'-dianhydride (5**):** $[\alpha]_{\text{D}}^{28} -152.2^\circ$ ($c=1.0$, CHCl_3); MS (FAB) m/z : 865 $[\text{M}+\text{H}]^+$, 887 $[\text{M}+\text{Na}]^+$; $^1\text{H-NMR}$ (400MHz, CDCl_3) δ : 3.61 (1H, dd, H-1a), 3.69 (1H, dd, H-6a), 3.77 (1H, dd, H-6b), 3.78 (1H, ddd, H-5), 3.87 (1H, d, H-1b), 3.93 (1H, dd, H-3), 4.04 (1H, dd, H-4); $J_{1a,1b} = 12.0$, $J_{3,4} = 10.0$, $J_{4,5} = 3.0$, $J_{5,6a} = 1.5$, $J_{5,6b} = 2.0$, $J_{6a,6b} = 12.5$ Hz; $^{13}\text{C-NMR}$ (100MHz, CDCl_3) δ : 61.61 (C-6), 64.08 (C-1), 71.62, 72.49, 74.60 ($3 \times \text{Ph-CH}_2$), 73.84 (C-5), 78.20 (C-4), 79.58 (C-3), 97.46 (C-2).

α -D-Fructopyranose β -D-fructopyranose 1,2':2,1'-dianhydride (6**):** A solution of **4** (115 mg, 0.133 mmol) in $\text{MeOH-H}_2\text{O}$ (4:1, 50 mL) containing AcOH (2.5 mL) was hydrogenolyzed in the presence of 10% Pd-C (250 mg) under an atmosphere of H_2 (310 kPa) for 24 h. The resulting mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo to give a syrup, which was purified by elution from a column of silica gel with CHCl_3 -MeOH (3:1 $\rightarrow$ 1:1 $\rightarrow$ 1:5, gradient). The major fraction was concentrated to give 48.4 mg (quantitative) of **6** as a colorless powder : mp 250°C (dec.) [lit.,¹ $250 \sim 270^\circ\text{C}$ (dec.)]; $[\alpha]_{\text{D}}^{28} -42.6^\circ$ ($c=1.0$, H_2O) [lit.,¹ -43.9° ($c=1.02$, H_2O)]; MS (FAB) m/z : 347 $[\text{M}+\text{Na}]^+$; $^1\text{H-NMR}$ (400MHz, $\text{D}_2\text{O} + \text{dioxane}$) δ : 3.46 (1H, d, H-1'a), 3.51 (1H, d, H-3'), 3.67 (1H, dd, H-6a), 3.68 (1H, dd, H-1a), 3.69 (1H, dd, H-6'a), 3.73 (1H, dd, H-6b), 3.76 (1H, d, H-3), 3.81 (1H, dd, H-6'b), 3.82 (1H, d, H-1b), 3.85 (1H, dd, H-4'), 3.86 (1H, dd, H-4), 3.98 (1H, ddd, H-5'), 4.00 (1H, ddd,

H-5), 4.13 (1H, dd, H-1'b) ; $J_{1a,1b} = 13.0$, $J_{3,4} = 4.0$, $J_{4,5} = 3.5$, $J_{5,6a} = 5.0$, $J_{5,6b} = 9.0$, $J_{6a,6b} = 11.5$, $J_{1'a,1'b} = 12.0$, $J_{3',4'} = 10.0$, $J_{4',5'} = 4.0$, $J_{5',6'a} = 2.0$, $J_{5',6'b} = 1.0$, $J_{6'a,6'b} = 13.0$ Hz ; ^{13}C -NMR (100MHz, D_2O + dioxane) δ : 62.27 (C-6), 63.36 (C-1'), 63.53 (C-1), 66.13 (C-6'), 66.50 (C-5), 71.10 (C-3'), 71.54 (C-3), 71.61 (C-5'), 73.14 (C-4'), 73.29 (C-4), 97.01 (C-2), 98.09 (C-2').

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