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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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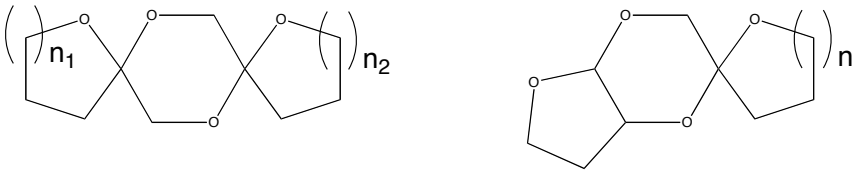
Abstract – α-D-Fructopyranose β-D-fructopyranose-1,2':2,1'- dianhydride has been stereoselectively synthesized by tandem catalytic glycosylation-spiroketalization of 3,4,5-tri-*O*-benzyl-β-D-fructo- pyranose. Of the several protic acid catalysts which exist, 0.3 molar equivalent trifluoromethane sulfonic 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 microorganisms[3] 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 sweetners[5] 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 thermolysis[9] or protonation[10] 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 developed[2] 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).



Type I : $n_1 = 1$, $n_2 = 1$
(α,α; β,β; α,β)

Type II : $n_1 = 1$, $n_2 = 2$
(α,α; β,β; α,β; β,α)

Type III : $n_1 = 2$, $n_2 = 2$
(β,β; α,β)

Type IV: n = 2
(β,β; β,α)

Type V: n = 1
(β,β; α,β)

Figure 1 Various kinds of di-D-fructose dianhydrids (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.

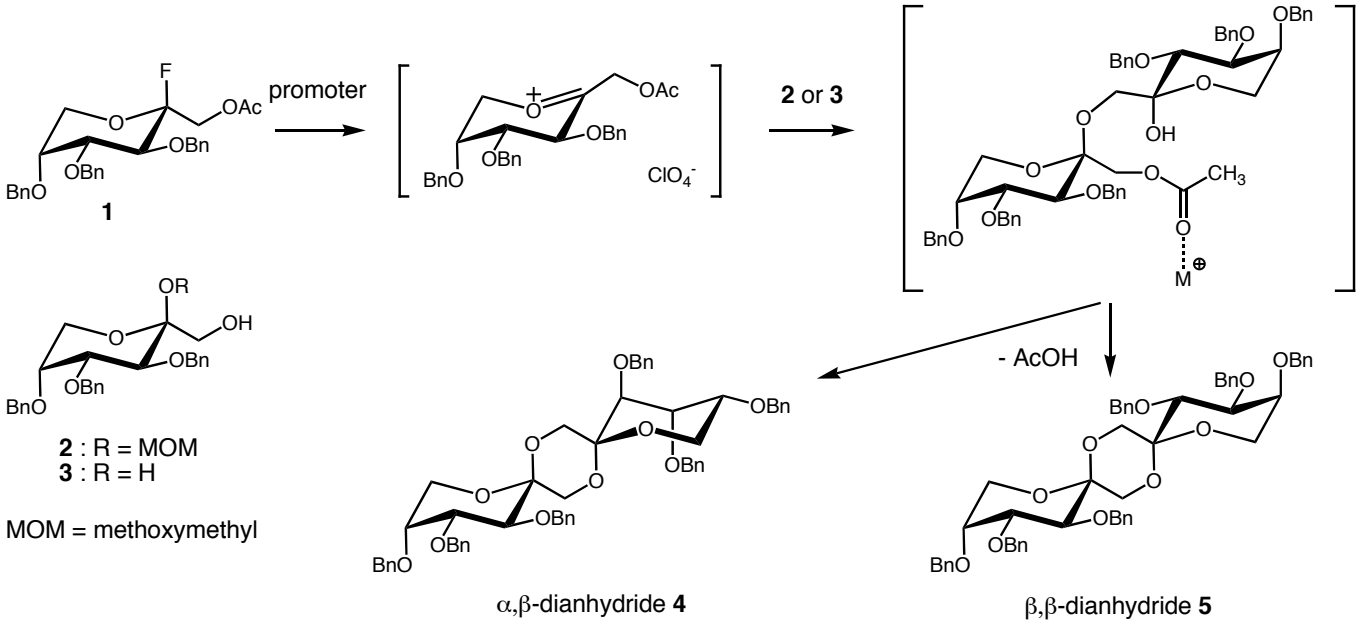
We herein propose an alternative method, i.e., an environmentally benign synthesis of α-D-fructopyranose β-D-fructopyranose-1,2':2,1'-dianhydride (**4**),[1,2] a Type III DFA, by catalytic, stereoselective glycosylation-spiroketalization of 3,4,5-tri-*O*-benzyl-β-D-fructo- pyranose (**3**) in 80% yield.

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→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, $SnCl_2$-$AgClO_4$,[13] Cp_2HfCl_2-$AgClO_4$,[14] and Cp_2HfCl_2–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 (eqiv.) [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_2ZrCl_2-$AgClO_4$ (1 – 1)	120	–
4	**1**	**3**	2.0	Cp_2HfCl_2-$AgClO_4$ (5 – 5)	5	quant.
5	**1**	**3**	2.0	Cp_2HfCl_2-AgOTf (5 – 5)	5	25
6	–	**3**	–	Cp_2HfCl_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.

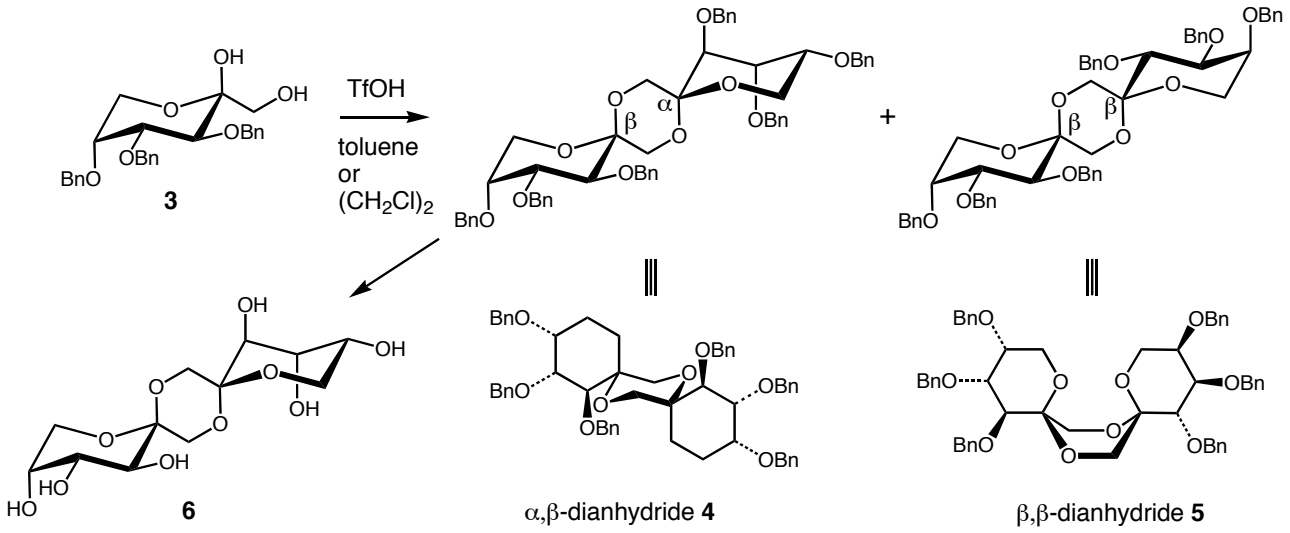


Scheme 1 Postulated reaction mechanism generating di-D-fructose dianhydrides (**4** and **5**)

When the fructosyl fluoride was reacted with 2-*O*-methoxymethyl 3,4,5-tri-*O*-benzyl-β-D-fructopyranoside[12] in the presence of $SnCl_2$-$AgClO_4$ 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 Cp_2HfCl_2-$AgClO_4$ 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 proposed[16] 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. (℃)	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)	$(CH_2Cl)_2$	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/H_2 in AcOH-MeOH-H_2O 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 CH_2Cl_2 (2 mL) with MS-4A (powder, 100 mg) were added $SnCl_2$ (9.4 mg, 0.05 mmol), $AgClO_4$ (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 CH_2Cl_2 (1 mL), filtered through a pad of Celite. The filtrate was washed with 5% aq. $NaHCO_3$ (10 mL) and water (3 x 10 mL), dried (Na_2SO_4), 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, $CHCl_3$) [lit.,[1] -59.0° (c=1.0, $CHCl_3$)]; MS (FAB) *m/z* : 865 $[M+H]^+$, 887 $[M+Na]^+$; ^{1}H-NMR (400MHz, $CDCl_3$) 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 ; ^{13}C-NMR (100MHz, $CDCl_3$) 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-$\underline{C}H_2$), 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-fructopyranse (**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 (quqntitative) 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): $[\alpha]_D^{28}$ -152.2° (c= 1.0, $CHCl_3$); MS (FAB) *m/z* : 865 $[M+H]^+$, 887 $[M+Na]^+$; ^{1}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}C-NMR(100MHz, $CDCl_3$) δ : 61.61 (C-6), 64.08 (C-1), 71.62, 72.49, 74.60 (3×Ph-$\underline{C}H_2$), 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 MeOH-H_2O (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→1:1→1:5, gradient). The major fraction was concentrated to give 48.4 mg (quantitative) of **6** as a colorless powder : mp 250℃ (dec.) [lit.,[1] 250 ～270℃ (dec.)]; $[\alpha]_D^{28}$ -42.6° (c=1.0, H_2O) [lit.,[1] -43.9° (c=1.02, H_2O)]; MS (FAB) *m/z* : 347 $[M+Na]^+$; ^{1}H-NMR (400MHz, D_2O + 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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