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Note

# A novel synthetic method for α-D-galactofuranose 1,2,5-orthopivalate

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**Abstract**

In order to synthesize (1→5)-β-D-galactofuranan by rig-opening polymerization, 3,6-di-*O*-benzyl-α-D-galactofuranose 1,2,5-orthopivalate (**9**) the most appropriate monomer was synthesized from D-galactose via 10 reaction steps. Novel intramolecular orthoesterification, which is a key reaction for sythesizing compound **9**, was accomplished by treatment of 5-*O*-monocholoacetyl-2,3,6-tri-*O*-pivaloyl-D-galactofuranosyl chloride (**6**) with thiourea in pyridine at 80 °C to give the expected orthoester (**7**) in good yield without any side reactions. 

*Keywords:* (1→5)-β-D-Galactofuranan; 3,6-Di-*O*-benzyl-α-D-galactofuranose 1,2,5-orthopivalate; 5-*O*-Chloroacetyl-2,3,6-tri-*O*-pivaloyl-D-galactofuranosyl chloride; Intramolecular orthoesterification

The (1→5)-β-D-galactofuranan structure is a component of extracellular polysaccharides produced by *Penicillium* and *Apergillus* species [1–3] and is recognized as an increasing cause of opportunistic infections in immunodeficient patients. The galactofuranosyl side chains have been found to be immunodominant [3]. In addition, (1→5)-linked β-D-galactofuranose oligosaccharides have been shown to inhibit the reaction of extracellular polysaccharides of *Penicillium* and *Aspergillus* species with antibodies [4]. It should also be noted that the fact that galactofuranose residues have not been found in mammalian glycoconjugates has implications for the design and use of artificial antigens. Therefore, the synthesis of (1→5)-β-linked galactofuranan may provide an useful model polysaccharide for biological and immunological studies.

For this purpose, several approaches to synthesize (1→5)-β-D-galactofuranan have been investigated. Step-by-step syntheses were suitable for synthesizing short oligosaccharide fragments of (1→5)-β-D-galactofuranan [5–8]. In addition, the trityl–cyanoethylidene polycondensation method was successfully applied to the synthesis of (1→5)-β-D-galactofuranan, resulting in a degree of polymerization (dp) of 25 [9].

On the other hand, we have previously reported the substituent effects on the stereoselective glycosylation in the synthesis of cellooligosaccharides [10–15]. The benzyl group at O-3 was found indispensable for obtaining β-linked glucosides stereospecifically in high yield, and the pivaloyl group at

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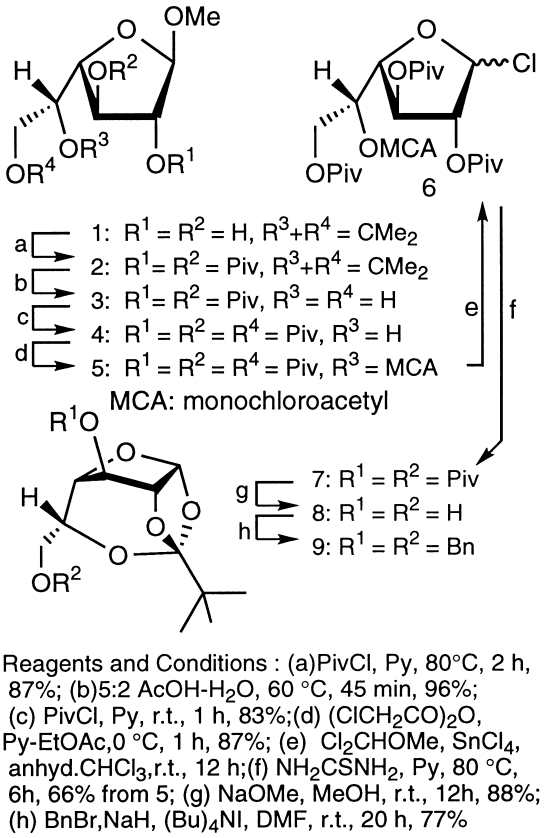
O-2 led to $\beta$-glycosidic linkages by the $\beta$-side attack of the glycosyl acceptor because of neighboring-group participation. Such substituent effects were nicely applied for the first chemical syntheses of 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→5)-$\beta$-D-glucofuranan from 1,4-anhydro-3,6-di-*O*-benzyl-2-*O*-pivaloyl-$\alpha$-D-glucopyranose [16] and 3,6-di-*O*-benzyl-2-*O*-pivaloyl-(1→4)-$\beta$-D-glucopyranan (cellulose derivative) from 3,6-di-*O*-benzyl-$\alpha$-D-glucopyranose 1,2,4-orthopivalate [17], respectively, by ring-opening polymerizations. On the basis of these results, we expected that there is a good possibility of synthesizing (1→5)-$\beta$-D-galactofuranan by the ring-opening polymerization of 3,6-di-*O*-benzyl-$\alpha$-D-galactofuranose 1,2,5-orthopivalate (**9**). Herein, we report a novel convenient synthesis of the orthoester derivative (**9**), the starting material for the synthesis of (1→5)-$\beta$-D-galactofuranan.

Several methods for synthesizing orthoester derivatives have been reported, althogh synthetic methods for the galactofuranose intramolecular orthoester derivatives such as compound **9** have not been reported to date. We initially tried to synthesize **9** by the previously reported procedures of Kochetkov et al. [18] and Nakatsubo et al. [17].

The Kochetkov method for $\beta$-L-arabinofuranose 1,2,5-orthobenzoate would force us to synthesize 1,2,3,5,6-penta-*O*-pivaloyl-D-galactofuranose in the first synthetic step. Pivaloylation of D-galactose carried out under several reaction conditions [19] always gave a mixture of 1,2,3,5,6-penta-*O*-pivaloyl-D-galactofuranose and 1,2,3,4,6-penta-*O*-pivaloyl-D-galactopyranose with approximately 1:2 ratio as determined by $^1$H NMR spectroscopic analysis. Furthermore, the separation of these isomers was not successfully accomplished by either recrystalization or silica gel column chromatography since they had almost the same $R_f$ values, i.e., 0.67 developed with 1:4 EtOAc–*n*-hexane.

On the other hand, 2,3,6-tri-*O*-pivaloyl-D-galactofuranose derived from compound **4** shown in Scheme 1 was treated with *N,N*′-carbonyldiimidazole in refluxing benzene according to the Nakatsubo method [17] to give compound **9** in less than 10% yield, because unexpected side reactions such as recyclization of the furanose to the pyranose occurred. Therefore, we investigated a novel synthetic procedure starting from the most appropriate precursor to give **9**.

Considering results obtained by the previous synthetic methods [17,18], we selected 5-*O*-chloroacetyl-2,3,6-tri-*O*-pivaloyl-D-galactofuranosyl chloride (**6**) as an appropriate precursor for **9**. The present key intermediate has the following special structural features: (*i*) the chlorine atom at C-1 more is stable than bromine and can likely be removed with thiourea or with a base such as pyridine; (*ii*) the chloroacetyl group at C-5 can be removed selectively with thiourea; (*iii*) the pivaloyl group at C-2 promotes the formation of the required dioxacarbenium ion by neighboring-group participation; (*iv*) no hydroxyl group is present at the anomeric position; hence, the rearrangement of furanose to pyranose does not occurr.




Reagents and Conditions : (a)PivCl, Py, 80°C, 2 h, 87%; (b)5:2 AcOH-$H_2O$, 60 °C, 45 min, 96%; (c) PivCl, Py, r.t., 1 h, 83%;(d) $(ClCH_2CO)_2O$, Py-EtOAc,0 °C, 1 h, 87%; (e) $Cl_2CHOMe$, $SnCl_4$, anhyd.$CHCl_3$,r.t., 12 h;(f) $NH_2CSNH_2$, Py, 80 °C, 6h, 66% from 5; (g) NaOMe, MeOH, r.t., 12h, 88%; (h) BnBr,NaH, $(Bu)_4NI$, DMF, r.t., 20 h, 77%

Scheme 1.

Thus, compound **6** was prepared by the synthetic route shown in Scheme 1. Methyl 5,6-*O*-isopropylidene-$\beta$-D-galactofuranoside (**1**), prepared by the reported methods [7,20], was treated with pivaloyl chloride in pyridine to afford **2**. The isopropylidene group was hydrolyzed with 5:2 acetic acid–water at 60 °C to afford **3**. The 6-*O*-pivaloyl group was introduced regioselectively by reacting **3** with a slight excess of pivaloyl chloride in pyridine at room temperature to afford **4** without any detectable 5-*O*-pivaloyl derivative, as determined by TLC. Chloroacetylation of **4** with chloroacetic anhydride in the presence of a catalytic amount of

pyridine in ethyl acetate at 0 °C afforded **5**, which was then converted into chloride **6** with dichloromethyl methyl ether and tin(IV) chloride in chloroform by the method of Richard and John [21].

Orhtoesterification of **6** was carried out with thiourea in pyridine at 80 °C according to a modification of the Cook and Maichuk method [22] applied to remove the chloroacetyl group. The following reaction mechanism may be proposed. The chlorine at C-1 is attracted to either thiourea or pyridine, and then the ester carbonyl group at O-2 attacks C-1 from the $\beta$-side to form a dioxacarbenium ion intermediate. Furthermore, the oxyanion arising from the cleavage of the chloroacetyl group at O-5 with thiourea attacks the dioxacarbenium ion, resulting in an intramolecular cyclization to give **7**.

Depivalation of **7** was followed by benzylation at O-3 and O-6 according to the coventional method to afford **9**. The structure of **9** was confirmed by both elemental and spectral analyses: IR (no carbonyl peak at 1740 $cm^{-1}$), $^1H$ NMR ($J_{1,2}$ 3.75 Hz and $J_{2,3} = J_{3,4}$ 0 Hz), and $^{13}C$ NMR (orthoester quaternary peak at $\delta$ 126 ppm, but no carbonyl peak).

In the synthetic route for **9** illustrated in Scheme 1, the key reaction is orthoestrerification of chloride **6**. This novel orthoesterification does not need a free hydroxyl group for the formation of the orthoester linkage. Therefore, the side reaction such as the conversion of furanose to pyranose and the formation of unexpected oligosaccharides does not occur. The preliminary-ring-opening polymerization of compound **9** was found to give stereoregular (1→5)-$\beta$-D-galactofuranan [23].

## 1. Experimental

*General*.—All melting points (mp) are uncorrected. $^1H$ NMR spectra and $^{13}C$ NMR spectra were recorded with a Bruker AC 300 FT NMR in chloroform-*d* with tetramethylsilane ($Me_4Si$) as the internal standard. Chemical shifts ($\delta$) and coupling constants (*J*) are given in $\delta$-values (ppm) and Hz, respectively. Optical rotations were measured using a JASCO Dip-1000 digital polarimeter. Anhydrous chloroform was distilled from $P_2O_5$.

*Methyl 5,6-*O*-isopropylidene-2,3-di-*O*-pivaloyl-*β*-*D*-galactofuranoside* (**2**).—To a solution of **1** (1.41 g, 6.04 mmol) [20] in pyridine (10 mL) was added pivaloyl chloride (1.79 mL, 14.5 mmol). The solution was stirred at 80 °C. After 2 h, methanol was added to the reaction mixture for the decomposition of excess pivaloyl chloride. The reaction mixture was diluted with ethyl acetate and washed with aqueous hydrochloric acid and brine. The organic phase was dried over $Na_2SO_4$, and concentrated in vacuo to give a yellow syrup that was purified on a silica gel column (Wakogel C-200, 1:4 EtOAc–n-hexane) to give compound **2** as a colorless syrup (2.12 g, 87.2%): $[\alpha]_D$ −37.5° (*c* 1.05, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.21, 1.22 (*s*, 18 H, piv-H), 1.34, 1.44 [*s*, 6 H, $C(CH_3)_2$], 3.41 (*s*, 3 H, $CH_3$), 3.84 (*dd*, 1 H, $J_{6a,6b}$ 8.42, $J_{5,6a}$ 6.46 Hz, H-6a), 4.06 (overlapped, 2 H, $J_{4,5}$ 5.21, $J_{5,6b}$ 6.68 Hz, H-4 and 6b), 4.34 (*quartet*, 1 H, H-5), 4.90 (*s*, 1 H, $J_{1,2}$ 0 Hz, H-1), 4.93 (*dd*, 1 H, $J_{3,4}$ 4.91 Hz, H-3), 4.97 (*d*, 1 H, $J_{2,3}$ 1.29 Hz, H-2); Anal. Calcd for $C_{20}H_{34}O_8$: C, 59.68; H, 8.52; O, 31.80. Found: C, 59.40; H, 8.38; O, 32.22.

*Methyl 2,3-di-*O*-pivaloyl-*β*-*D*-galactofuranoside* (**3**).—Compound **2** (1.06 g, 2.63 mmol) was dissolved in 5:2 acetic acid–water and stirred at 60 °C. After 45 min, the reaction mixture was concentrated in vacuo to give compound **3** as a yellow syrup (919 mg, 96.5%): $[\alpha]_D$ −39.0° (*c* 1.01, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.21, 1.22 (*s*, 18 H, piv-H), 3.99 (*s*, 3 H, $CH_3$ H), 3.7–4.0 (overlapped 3 H, H-5, 6a and 6b), 4.07 (*t*, 1 H, $J_{4,5}$ 3.79 Hz, H-4), 4.91 (*s*, 1 H, $J_{1,2}$ 0 Hz, H-1), 5.05 (*d*, 1 H, $J_{2,3}$ 1.60 Hz, H-2), 5.07 (*dd*, 1 H, $J_{3,4}$ 4.46 Hz, H-3); Anal. Calcd for $C_{17}H_{30}O_8$: C, 56.34; H, 8.34; O, 35.32. Found: C, 56.09; H, 8.50; O, 35.41.

*Methyl 2,3,6-tri-*O*-pivaloyl-*β*-*D*-galactofuranoside* (**4**).—To a solution of **3** (1.94 g, 5.36 mmol) in pyridine (10 mL) was added pivaloyl chloride (726 mL, 5.89 mmol). The solution was stirred at room temperature for 1 h. The reaction mixture was worked up in the same manner as that described for the synthesis of compound **2**. Compound **4** was crystallized from n-hexane (1.96 g, 83.4%): mp 103 °C; $[\alpha]_D$ −39.8° (*c* 0.99, $CHCl_3$); $^1H$ NMR ($CDCl_3$): $\delta$ 1.21 (*s*, 27 H, piv-H), 3.38 (*s*, 3 H, $CH_3$), 4.01 (*dd*, 1 H, $J_{4,5}$ 2.19 Hz, H-4), 4.1–4.3 (overlapped, 3 H, $J_{6a,6b}$ 12.96, $J_{5,6a}$ 5.15, $J_{5,6b}$ 8.51 Hz, H-5, 6a and 6b), 4.90 (*s*, 1 H, $J_{1,2}$ 0 Hz, H-1), 5.04 (*d*, 1 H, $J_{2,3}$ 1.45 Hz, H-2), 4.87 (*dd*, 1 H, $J_{3,4}$ 4.87 Hz, H-3); Anal. Calcd for $C_{22}H_{38}O_9$: C, 59.17; H, 8.58; O, 32.25. Found: C, 59.07; H, 8.56; O, 32.37.

*Methyl 5-*O*-chloroacetyl-2,3,6-tri-*O*-pivaloyl-*β*-*D*-galactofuranoside* (**5**).—To a solution of **4** (1.40 g, 3.29 mmol) in ethyl acetate (30 mL) was added monochloroacetic anhydride (6.74 g, 39.4 mmol) and pyridine (6.65 mL, 82.3 mmol). The solution

was stirred at 0 °C for 1 h. The reaction mixture was diluted with ethyl acetate and washed with water and brine. The organic phase was dried over $Na_2SO_4$, and concentrated in vacuo to give a yellow syrup that was purified on a silica gel column (Wakogel C-200, 1:4 EtOAc–*n*-hexane) to give compound **5** as a colorless syrup (1.50 g, 87.2%): $[\alpha]_D$ −25.5° (*c* 1.01, $CHCl_3$); $^1$H NMR ($CDCl_3$): δ 1.19, 1.20, 1.23 (*s*, 27 H, Piv-H), 3.38 (*s*, 3 H, $CH_3$), 4.10 (*s*, 2 H, $ClCH_2CO$), 4.19 (*dd*, 1 H, $J_{5,6a}$ 7.63, $J_{6a,6b}$ 12.07 Hz, H-6a), 4.22 (*t*, 1 H, $J_{4,5}$ 5.27 Hz, H-4), 4.46 (*dd*, 1 H, $J_{5,6b}$ 3.78 Hz, H-6b), 4.86 (*s*, 1 H, $J_{1,2}$ 0 Hz, H-1), 5.00 (*dd*, 1 H, $J_{3,4}$ 5.27 Hz, H-3), 5.01 (*d*, 1 H, $J_{2,3}$ 1.85 Hz, H-2), 5.44 (*m*, 1 H, 5-H); Anal. Calcd for $C_{24}H_{39}ClO_{10}$: C, 55.12; H, 7.46; O, 30.63; Cl, 6.79. Found: C, 55.05; H, 7.71; O, 30.6; Cl, 6.65.

*3,6-Di*-O-*pivaloyl*-α-D-*galactofuranose 1,2,5-orthopivalate* (**7**).—To a solution of **5** (682 mg, 1.31 mmol) in anhydrous chloroform (6 mL) was added dichloromethyl methyl ether (2.37 mL, 26.2 mmol) and tin(IV) chloride (1.02 μL, 0.873 mmol). The solution was stirred at room temperature for 12 h. The reaction mixture was diluted with ethyl acetate and sequentially washed with cold water, saturated $NaHCO_3$, and brine. The organic phase was concentrated in vacuo to give compound **6** as a crude oil (685 mg). To a solution of crude **6** (685 mg) in pyridine (30 mL) was added thiourea (298 mg, 391 mmol). The solution was stirred at 80 °C for 6 h. The reaction mixture was diluted with ethyl acetate and washed with water and brine. The organic phase was concentrated in vacuo to give a brown powder that was purified on a silica gel column eluted with chloroform and crystalized from methanol to give compound **7** as colorless crystals (360 mg, 66.3%): mp 134 °C; $[\alpha]_D$ +71.3° (*c* 1.02, $CHCl_3$); $^1$H NMR ($CDCl_3$): δ 1.02, 1.20 (*s*, 27 H, piv-H), 4.15 (*m*, 1 H, H-5), 4.21–4.25 (overlapped, 2 H, H-6a,6b), 4.40 (*t*, 1 H, $J_{4,5}$ 1.80 Hz, H-4), 4.55 (*dd*, 1 H $J_{2,3}$ 0 Hz, $J_{2,4}$ 1.49, H-2), 5.13 (*s*, 1 H, $J_{3,4}$ 0 Hz, H-3), 5.90 (*d*, 1 H, $J_{1,2}$ 3.77, H-1); $^{13}$C NMR ($CDCl_3$): δ 103.4 (C-1), 63.9, 74.8, 78.3, 81.0, 81.1 (C-2, 3, 4, 5, 6), 24.9, 27.0, 27.1 (Me–C), 37.3, 38.3 [$C(CH_3)$], 126.6 (orthoester quaternary carbon), 177.6, 178.0 (carbonyl); Anal. Calcd for $C_{21}H_{34}O_8$: C, 60.85; H, 8.27; O, 30.88. Found: C, 60.82; H, 8.22; O, 30.96.

α-D-*Galactofuranose 1,2,5-orthopivalate* (**8**).—To a solution of **7** (130 mg, 0.314 mmol) in methanol (5 mL) was added 28% NaOMe in methanol (1.12 mL, 4.71 mmol). The solution was stirred at room temperature for 12 h. The reaction mixture was neutralized with acetic acid and concentrated in vacuo The residue was dissolved in chloroform and washed with water and brine. The organic phase was dried over $Na_2SO_4$ and concetrated in vacuo to give a colorless powder that was purified on a silica gel column eluted with chloroform and crystalized from methanol to give compound **8** as colorless crystals (68.0 mg, 88.0%): mp 111 °C; $[\alpha]_D$ +24.4° (*c* 1.00, $CHCl_3$); Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37; O, 38.98. Found: C, 53.74; H, 7.30; O, 38.96.

*3,6-Di*-O-*benzyl*-α-D-*galactofuranose 1,2,5-orthopivalate* (**9**).—Compound **8** (65.4 mg, 0.266 mmol) was dissolved in $Me_2NCHO$ (3 mL). Sodium hydride (25.5 mg, 0.638 mmol, 60% in mineral oil) and tetra-*n*-butyl ammonium iodide (23.5 mg, 0.0638 mmol) were added, followed by the slow addition of benzyl bromide (75.8 μL, 0.638 mmol) at 0 °C . The solution was stirred at room temperature for 20 h. Methanol was then added to the reaction mixture for the decomposition of excess benzyl bromide. The reaction mixture was worked up by the same manner as that of compound **5**. Crude compound **9** was purified on a silica gel column eluted with chloroform to give compound **9** as a colorless syrup (88.1 mg, 77.7%): $[\alpha]_D$ +38.8° (*c* 0.95, $CHCl_3$); $^1$H NMR ($CDCl_3$): δ 0.98 (*s*, 9 H, piv-H), 3.57 (*dd*, 1 H, $J_{5,6a}$ 5.61, $J_{6a,6b}$ 8.50 Hz, H-6a), 3.72 (*t*, 1 H, $J_{5,6b}$ 8.50 Hz, H-6b), 3.96 (*m*, 1 H, H-5), 4.07 (*s*, 1 H, $J_{3,4}$ 0 Hz, H-3), 4.51, 4.57, 4.60 (*d*, *d*, *s*, 1 H, 1 H, 2 H, respectively, benzyl-H), 4.58 (*dd*, 1 H, $J_{2,3}$ 0, $J_{2,4}$ 1.50 Hz, H-2), 4.65 (*t*, 1 H, $J_{4,5}$ 1.89 Hz H-4), 5.90 (*d*, 1 H, $J_{1,2}$ 3.75 Hz, H-1), 7.33 (*s*, 5 H, AH); $^{13}$C NMR ($CDCl_3$): δ 103.4 (C-1), 69.8, 71.5, 73.5, 75.9, 80.3, 80.9, 84.1 (C-2, 3, 4, 5, 6 and benzyl-C), 25.0 ($CH_3$), 37.3 [$C(CH_3)$], 126.3 (orthoester quaternary carbon); Anal. Calcd for $C_{25}H_{30}O_6$: C, 70.40; H, 7.09; O, 22.51. Found: C, 70.12; H, 7.13; O, 22.75.

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