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Note

Synthesis of *C*-pentopyranosylphloroacetophenone derivatives and their anomerization

Toshihiro Kumazawa,* Tomoki Saito, Shigeru Matsuba, Shingo Sato, Jun-ichi Onodera

Department of Chemistry and Chemical Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa-shi, Yamagata 992-8510, Japan

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Abstract

A 3-*C*-β-D-xylopyranosylphloroacetophenone derivative was synthesized via reaction of 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl fluoride and 2,4-di-*O*-benzylphloroacetophenone in the presence of boron trifluoride diethyl etherate. Alternatively, the reaction of 2,3,4-tri-*O*-benzyl-β-L-arabinopyranosyl fluoride with 2,4-di-*O*-benzylphloroacetophenone afforded both the 3-*C*-α-L- and the 3-*C*-β-L-arabinopyranosylphloroacetophenone derivatives under identical reaction conditions. The *C*-β-L-arabinoside, the thermodynanic product, was produced via anomerization of the *C*-α-L-arabinoside, the kinetic product during the reaction. The composition of this product mixture is apparently dictated by both 1,3-diaxial and 2,4-diaxial interactions.

Keywords: *C*-Glycosylic compound; *C*-Glycosylflavonoid; *C*-β-D-Xyloside; *C*-α-L-Arabinoside; *C*-β-L-Arabinoside; Diaxial interaction

The chemistry of aryl *C*-glycosylic compounds, including their synthesis [1], has been the subject of considerable attention recently because of their biological activities [2]. A number of flavonoids contain aryl *C*-glycosyl moieties as part of their structures and include the naturally occurring *C*-glycosyl flavonoids [3]. In this laboratory, our interests are in the synthesis of the glycosylic portion of *C*-glycosyl flavonoids. During the course of our synthetic study on *C*-glycosyl flavonoids, we prepared some *C*-glycosylphloroacetophenone derivatives, that contain D-glucosyl, D-galactosyl, D-mannosyl, or 2-deoxy-D-*arabino*-hexosyl moieties, respectively, as the glycosyl moiety, [4]. A D-glucosyl residue constitutes the sugar moiety in the majority 67% of the *C*-glycosyl flavonoids, which include mono-*C*-glycosyl flavonoids, di-*C*-glycosyl flavonoids, and *C*-glycosyl flavonoid *O*-glycosides. Among the *C*-glycosyl flavonoids, those that contain an L-arabinosyl or a D-xylosyl moiety are much less common. The L-arabinosyl moiety comprises 17%, and the D-xylosyl moiety 4% of the total number of sugar moieties in *C*-glycosyl flavonoids [3]. We describe herein the synthesis of a 3-*C*-β-D-xylopyranosylphloroacetophenone derivative **3**, which was prepared in an anomerically pure form, in

* Corresponding author. Tel.: +81-238-263122; fax: +81-238-263413.

E-mail address: tk111@dip.yz.yamagata-u.ac.jp (T. Kumazawa).

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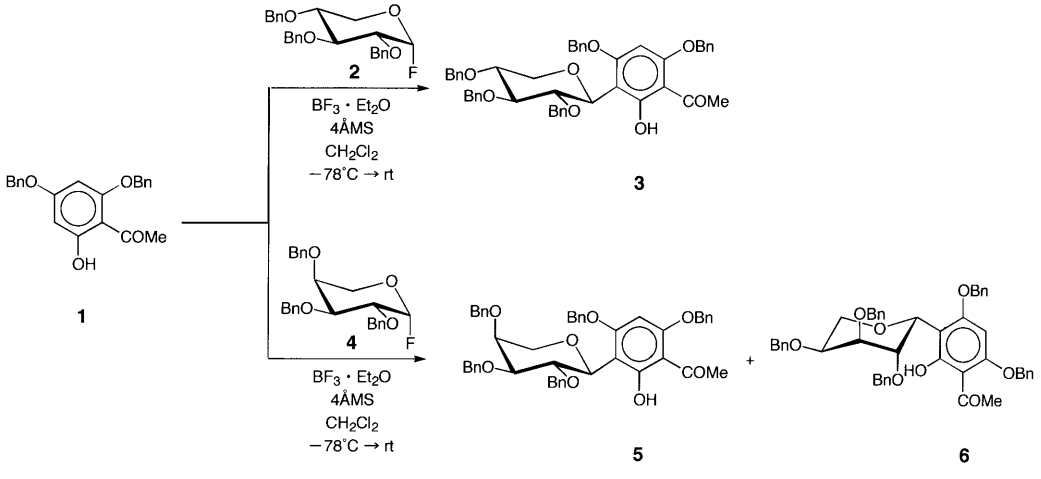
the presence of boron trifluoride diethyl etherate. We also report the synthesis of a 3-*C*-α-L-arabinopyranosylphloroacetophenone derivative **5**, which is the kinetic product, and a 3-*C*-β-L-arabinopyranosylphloroacetophenone derivative **6**, the thermodynamic product under identical conditions.

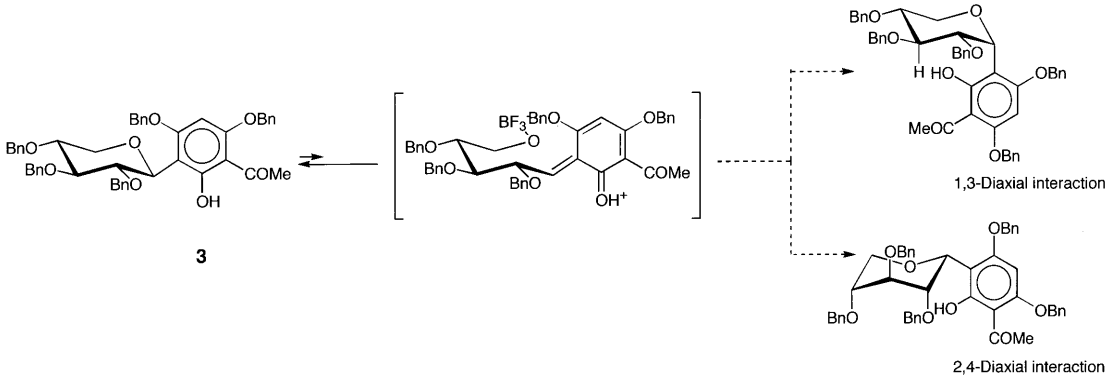
3-*C*-β-D-Xylopyranosylphloroacetophenone derivative **3** was synthesized according to methods described previously [4]. The reaction of 2,4-di-*O*-benzyl phloroacetophenone **1** with 2,3,4-tri-*O*-benzyl-β-D-xylopyranosyl fluoride **2** [5] in the presence of boron trifluoride diethyl etherate gave the 3-*C*-β-D-xylopyranosylphloroacetophenone derivative **3** in 81% yield, in anomerically pure form, via an $O \rightarrow C$ glycoside rearrangement (Scheme 1). The initial reaction temperature of -78 °C was slowly elevated to ambient temperature. The ^{1}H NMR spectrum showed that the *C*-β-D-xyloside **3** adopted the $^4C_1$ conformation at a temperature of 140 °C. The NMR experiment was conducted at elevated temperature because the structural assignment by NMR spectroscopy at ambient temperature was hampered by the slow rotation around the C-1–aglycon bond. Even at elevated reaction temperature, the *C*-β-D-xyloside **3** could not be anomerized to the α-isomer by the Lewis acid, boron trifluoride diethyl etherate, in the course of the reaction. In addition, neither the *C*-glucosyl-, *C*-galactosyl-, nor *C*-2-deoxy-*arabino*-hexosylphloroacetophenone derivatives, which we have previously prepared [4], could be anomerized under these conditions.

On the other hand, the reaction of 2,4-di-*O*-benzyl phloroacetophenone **1** with 2,3,4-tri-*O*-benzyl-β-L-arabinopyranosyl fluoride **4** in the presence of boron trifluoride diethyl etherate gave the 3-*C*-α-L-arabinopyranosylphloroacetophenone derivative **5** in 52% yield and the 3-*C*-β-L-arabinopyranosylphloroacetophenone derivative **6** in 18% yield under identical conditions as mentioned above. Thin-layer chromatography (TLC) of the reaction mixture indicated that the *C*-α-L-arabinoside **5**, the kinetic product, was produced via an $O \rightarrow C$ glycoside rearrangement at low temperature and that the resulting *C*-α-L-arabinoside **5** was then anomerized to give the *C*-β-L-arabinoside **6** as the thermodynamic product by boron trifluoride diethyl etherate at temperatures greater than -20 °C. The ^{1}H NMR showed that the *C*-α-L-arabinoside **5** adopted the $^4C_1$ conformation, and that the *C*-β-L-arabinoside **6** adopted $^1C_4$ conformation. The NMR experiment with the *C*-α-L-arabinoside **5** was conducted at elevated temperature for reasons mentioned above. To the best of our knowledge, there are no reports on the isolation of *C*-β-L-arabinosyl flavonoids. One report exists that reports that the *C*-α-L-arabinosyl flavone was anomerized by acid treatment in water to give the *C*-β-L-arabinosyl flavones [6].

Such an anomerization process has been discussed by Suzuki and co-workers [7] and Schmidt [8], respectively. In this present study, even if boron trifluoride diethyl etherate weakened the C-1–O bond by attack at the tetra-



Scheme 1.



Scheme 2.

hydropyran oxygen, which leads to an open chain intermediate that might undergo isomerization and subsequent recyclization, the *C*-β-D-xyloside **3** could not give rise to a *C*-α-D-xyloside. While the conversion of the *C*-β-D-xyloside **3** to the *C*-α-D-xyloside isomer with a $^4C_1$ conformation would not be expected because of unfavorable 1,3-diaxial interactions, and the conversion of **3** to the *C*-α-D-xyloside isomer with a $^1C_4$ conformation would not be expected because of unfavorable 2,4-diaxial interactions, the *C*-β-L-arabinoside **6** with a $^1C_4$ conformation does not have such severe steric effects (Scheme 2). Therefore the *C*-α-L-arabinoside **5** can be anomerized to give the *C*-β-L-arabinoside **6** with a $^1C_4$ conformation via Lewis acid. These facts are typical comparative examples that can be used to explain the diaxial interactions.

Syntheses of *C*-glycosylphloroacetophenone derivatives that possess a rare sugar, which are partial structures of naturally occurring *C*-glycosyl flavonoids, including their anomerization, are currently under way.

1. Experimental

General methods.—All non-aq reactions were carried out under an atmosphere of dry Ar using freshly distilled solvents, unless otherwise noted. All reactions were monitored by TLC, which was carried out on 0.25 mm Silica Gel 60 F_{254} plates (E. Merck) using either UV light, a 5% ethanolic soln of ferric chloride or a 5% ethanolic soln of phosphomolybdic acid with heat as developing agents. Wakogel C-300® (particle size 0.045–0.075 mm) was used for column chromatography. Melting points are uncorrected. Optical rotations were recorded using $CHCl_3$ as solvent on a JASCO DIP-370 digital polarimeter. IR spectra were recorded on a Horiba FT-200 IR spectrometer as KBr pellets or as films on NaCl plates. Mass spectra were recorded on a JEOL JMS-AX-505-HA mass spectrometer under conditions of electron impact (EI) or fast-atom bombardment (FAB) using 3-nitrobenzyl alcohol as the matrix. ^{1}H NMR spectra were recorded on Varian Inova 500 instrument using Me_4Si as the internal reference.

2,3,4-Tri-O-*benzyl*-α-D-*xylopyranosyl fluoride* (**2**).—Compound **2** was synthesized according to Noyori's method [5] and isolated as colorless crystals: mp 66 °C; $[\alpha]_D^{25}$ +6.0° (*c* 1.0, $CHCl_3$); R_f 0.75 (3:1 hexane–EtOAc); IR (KBr): 3088, 3064, 3030, 3001, 2953, 2922, 2902, 2885, 2863, 2850, 2843, 1951, 1867, 1811, 1738, 1605, 1582, 1497, 1474, 1454, 1375, 1362, 1348, 1333, 1213, 1174, 1159, 1136, 1101, 1074, 1030, 953, 947, 889, 764, 743, 731, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 3.46 (ddd, 1 H, *J* 2.7, 9.5, 25.6 Hz, H-2), 3.61 (ddd, 1 H, *J* 5.6, 9.5, 11.0 Hz, H-4), 3.69 (t, 1 H, *J* 11.0 Hz, H-5a), 3.77 (dd, 1 H, *J* 5.6, 11.0 Hz, H-5b), 3.91 (t, 1 H, *J* 9.5 Hz, H-3), 4.63 (d, 1 H, *J* 11.6 Hz, benzylic CH_2), 4.69 (d, 1 H, *J* 11.8 Hz, benzylic CH_2), 4.75 (d, 1 H, *J* 11.6 Hz, benzylic CH_2), 4.80 (d, 1 H, *J* 11.8 Hz, benzylic CH_2), 4.91 (s, 2 H, benzylic CH_2), 5.45 (dd, 1 H, *J* 2.7, 53.2 Hz, H-1), 7.27–7.37 (m, 15 H, ArH); EIMS: *m*/*z* 422 [M$^+$]. Anal. Calcd for $C_{26}H_{27}FO_4$: C, 73.91; H, 6.44. Found: C, 73.86; H, 6.47.

*4,6-Bis-benzyloxy-2-hydroxy-3-*C*-(2,3,4-tri-*O*-benzyl-β-*D*-xylopyranosyl)acetophenone* (**3**).—To a stirred mixture of **1** (3.71 g 10.7 mmol, 3 equiv), 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl fluoride (**2**, 1.50 g, 3.55 mmol) and powdered 4 Å molecular sieves (4 g) in CH_2Cl_2 (50 mL) at −78 °C, $BF_3{\cdot}Et_2O$ (960 μL, 7.81 mmol, 2.2 equiv) was added dropwise, and the mixture was stirred for 30 min. The temperature was then allowed to increase to −42 °C with continued stirring for 0.5 h, then to −20 °C for 1 h, and finally to rt for 1 h. After adding water, the resulting mixture was filtered through a Celite® pad. The filtrate was extracted with $CHCl_3$, and the organic layer was washed with water and brine and then dried over anhyd $MgSO_4$. The solvent was evaporated in vacuo. The residual syrup was column chromatographed on silica gel (5:1 hexane–EtOAc) to give **3** (2.17 g, 81%) as a colorless, highly viscous oil: $[\alpha]_D^{25}$ −24° (*c* 1.0, $CHCl_3$); R_f 0.50 (3:1 hexane–EtOAc); IR (NaCl): 3088, 3062, 3030, 2929, 2912, 2873, 1954, 1876, 1809, 1622, 1597, 1497, 1454, 1429, 1367, 1273, 1203, 1167, 1117, 1092, 1028, 1001, 985, 908, 797, 737, 698 cm^{-1}; ^1H NMR (Me_2SO-d_6 at 140 °C): δ 2.51 (s, 3 H, ArAc), 3.16 (dd, 1 H, *J* 10.5, 11.2 Hz, H-5′a), 3.52–3.57 (m, 2 H, H-3′,4′), 4.00 (dd, 1 H, *J* 4.6, 11.2 Hz, H-5′b), 4.16 (d, 1 H, *J* 11.5 Hz, benzylic CH_2), 4.27 (t, 1 H, *J* 9.5 Hz, H-2′), 4.45 (d, 1 H, *J* 11.5 Hz, benzylic CH_2), 4.62 (s, 2 H, benzylic CH_2), 4.75 (d, 1 H, *J* 11.7 Hz, benzylic CH_2), 4.77 (d, 1 H, *J* 9.5 Hz, H-1′), 4.81 (d, 1 H, *J* 11.7 Hz, benzylic CH_2), 5.14 (s, 2 H, benzylic CH_2), 5.24 (s, 2 H, benzylic CH_2), 6.39 (s, 1 H, ArH), 6.87–7.46 (m, 25 H, ArH), 13.74 (br,s, 1 H, ArOH); FABMS (positive): *m*/*z* 751 $[M+H]^+$; FABMS (negative ion): *m*/*z* 749 $[M-H]^-$. Anal. Calcd for $C_{48}H_{46}O_8$: C, 76.78; H, 6.17. Found: C, 76.48; H, 6.32.

*2,3,4-Tri-*O*-benzyl-β-L-arabinopyranosyl fluoride* (**4**).—Compound **4** was synthesized according to Noyori's method [5] and isolated as colorless crystals: mp 38°C; $[\alpha]_D^{25}$ +37° (*c* 1.0, $CHCl_3$); R_f 0.69 (3:1 hexane–EtOAc); IR (KBr): 3089, 3064, 3032, 3008, 2978, 2937, 2927, 2906, 2870, 1497, 1454, 1365, 1356, 1171, 1149, 1128, 1105, 1082, 1049, 1028, 1014, 1003, 987, 926, 885, 843, 775, 743, 696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.79 (d, 1 H, *J* 12.6 Hz, H-5a), 3.81 (m, 1 H, H-4), 3.85 (dd, 1 H, *J* 2.0, 12.6 Hz, H-5b), 3.90 (dd, 1 H, *J* 3.2, 10.0 Hz, H-3), 4.04 (ddd, 1 H, *J* 2.7, 10.0, 24.9 Hz, H-2), 4.66 (d, 1 H, *J* 12.0 Hz, benzylic CH_2), 4.73 (s, 2 H, benzylic CH_2), 4.737 (d, 1 H, *J* 11.7 Hz, benzylic CH_2), 4.743 (d, 1 H, *J* 12.0 Hz, benzylic CH_2), 4.89 (d, 1 H, *J* 11.7 Hz, benzylic CH_2), 5.61 (dd, 1 H, *J* 2.7, 53.8 Hz, H-1), 7.23–7.39 (m, 15 H, ArH); EIMS: *m*/*z* 422 $[M^+]$. Anal. Calcd for $C_{26}H_{27}FO_4$: C, 73.91; H, 6.44. Found: C, 73.72; H, 6.37.

*4,6-Bis-benzyloxy-2-hydroxy-3-*C*-(2,3,4-tri-*O*-benzyl-α-L-arabinopyranosyl)acetophenone* (**5**) *and 4,6-bis-benzyloxy-2-hydroxy-3-*C*-(2,3,4-tri-*O*-benzyl-β-L-arabinopyranosyl)-acetophenone* (**6**).—To a stirred mixture of **1** (2.78 g, 7.98 mmol, 3 equiv), 2,3,4-tri-*O*-benzyl-β-L-arabinopyranosyl fluoride (**4**, 1.12 g, 2.66 mmol) and powdered 4 Å molecular sieves (3.5 g) in CH_2Cl_2 (40 mL) at −78 °C, $BF_3{\cdot}Et_2O$ (690 μL, 5.59 mmol, 2.1 equiv) was added dropwise, and the mixture then stirred for 0.5 h. The temperature was allowed to increase to −42 °C, and the stirring was continued for 0.5 h, then to −20 °C for 1 h, and finally to rt for 1 h. After adding water, the resulting mixture was filtered through a Celite® pad. The filtrate was extracted with $CHCl_3$, and the organic layer was washed with water and brine and then dried over anhyd $MgSO_4$. The solvent was evaporated in vacuo, and the resulting syrup was chromatographed on a silica gel column (5:1 hexane–EtOAc) to give **5** (1.04 g, 52%) as a colorless, highly viscous oil and **6** (0.35 g, 18%) as a colorless, viscous oil:

*4,6-Bis-benzyloxy-2-hydroxy-3-*C*-(2,3,4-tri-*O*-benzyl-α-L-arabinopyranosyl)acetophenone* (**5**).—$[\alpha]_D^{25}$ +2.2° (*c* 1.0, $CHCl_3$); R_f 0.39 (3:1 hexane–EtOAc); IR (NaCl): 3088, 3062, 3030, 3007, 2945, 2931, 2872, 1956, 1878, 1811, 1734, 1618, 1593, 1497, 1454, 1429, 1385, 1367, 1352, 1271, 1228, 1205, 1165, 1113, 1099, 1028, 1003, 910, 849, 797, 735, 696 cm^{-1}; ^1H NMR (Me_2SO-d_6 at 100 °C): δ 2.50 (s, 3 H, ArAc), 3.39 (d, 1 H, *J* 12.6 Hz, H-5′a), 3.64 (dd, 1 H, *J* 3.4, 9.2 Hz, H-3′), 3.94 (m, 1 H, H-4′), 4.04 (dd, 1 H, *J* 2.0, 12.6 Hz, H-5′b), 4.17 (d, 1 H, *J* 11.5 Hz, benzylic CH_2), 4.52

(d, 1 H, *J* 11.5 Hz, benzylic CH_2), 4.59 (d, 1 H, *J* 12.1 Hz, benzylic CH_2), 4.631 (d, 1 H, *J* 12.4 Hz, benzylic CH_2), 4.637 (dd, 1 H, *J* 9.2, 9.8 Hz, H-2′), 4.66 (d, 1 H, *J* 12.1 Hz, benzylic CH_2), 4.67 (d, 1 H, *J* 12.4 Hz, benzylic CH_2), 4.72 (d, 1 H, *J* 9.8 Hz, H-1′), 5.15 (s, 2 H, benzylic CH_2), 5.20 (d, 1 H, *J* 12.6 Hz, benzylic CH_2), 5.22 (d, 1 H, *J* 12.6 Hz, benzylic CH_2), 6.38 (s, 1 H, ArH), 6.89–7.47 (m, 25 H, ArH), 13.49 (br.s, 1 H, ArOH); FABMS (positive): *m*/*z* 751 $[M+H]^+$; FABMS (negative ion): *m*/*z* 749 $[M-H]^-$. Anal. Calcd for $C_{48}H_{46}O_8$: C, 76.78; H, 6.17. Found: C, 76.58; H, 6.10.

*4,6-Bis-benzyloxy-2-hydroxy-3-*C*-(2,3,4-tri-*O*-benzyl-β-*L*-arabinopyranosyl)acetophenone* (**6**).—$[\alpha]_D^{25}$ −72° (*c* 1.0, $CHCl_3$); R_f 0.48 (3:1 hexane–EtOAc); IR (NaCl): 3311, 3088, 3062, 3030, 3007, 2929, 2919, 2873, 1954, 1876, 1811, 1697, 1618, 1595, 1497, 1454, 1427, 1375, 1348, 1273, 1157, 1097, 1076, 1028, 910, 750, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.53 (s, 3 H, ArAc), 3.63 (dd, 1 H, *J* 1.5, 3.8 Hz, H-2′), 3.85 (m, 1 H, H-3′), 3.87 (t, 1 H, *J* 11.9 Hz, H-5′a), 4.00–4.04 (m, 2 H, H-4′, H-5′b), 4.14 (d, 1 H, *J* 12.1 Hz, benzylic CH_2), 4.23 (d, 1 H, *J* 12.1 Hz, benzylic CH_2), 4.44 (d, 1 H, *J* 12.7 Hz, benzylic CH_2), 4.47 (d, 1 H, *J* 12.7 Hz, benzylic CH_2), 4.50 (d, 1 H, *J* 12.8 Hz, benzylic CH_2), 4.53 (d, 1 H, *J* 12.8 Hz, benzylic CH_2), 4.88 (d, 1 H, *J* 11.6 Hz, benzylic CH_2), 4.92 (d, 1 H, *J* 11.6 Hz, benzylic CH_2), 5.05 (d, 1 H, *J* 12.1 Hz, benzylic CH_2), 5.07 (d, 1 H, *J* 12.1 Hz, benzylic CH_2), 5.39 (d, 1 H, *J* 1.5 Hz, H-1′), 6.00 (s, 1 H, ArH), 6.92–7.43 (m, 25 H, ArH), 11.56 (br,s, 1 H, ArOH). The NOESY spectrum of **6** indicated a correlation between H-1′ and H-5′a (axial), as well as H-2′; FABMS (positive): *m*/*z* 751 $[M+H]^+$; FABMS (negative ion): *m*/*z* 749 $[M-H]^-$. Anal. Calcd for $C_{48}H_{46}O_8$: C, 76.78; H, 6.17. Found: C, 76.59; H, 6.12.

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