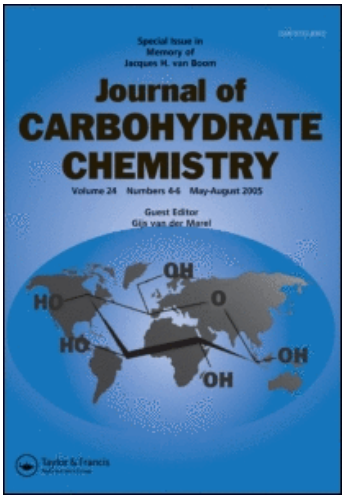

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Synthesis of and Glycosidation by 2-Deoxy-2-Fluoro-D-Mannopyranose

Tomoya Ogawa[a]; Yukio Takahashi[a]
[a] The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama, Japan

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SYNTHESIS OF AND GLYCOSIDATION BY 2-DEOXY-2-FLUORO-D-MANNOPYRANOSE

Tomoya Ogawa* and Yukio Takahashi

The Institute of Physical and Chemical Research (RIKEN),
Wako-shi, Saitama, 351, Japan

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With the increased biochemical interests of fluorocarbohydrates, several approaches have been establised toward the synthesis of 2-deoxy-2-fluorocarbohydrates by taking advantage of the ease of the addition reaction to readily available peracetylated glycals by employing either CF_3OF,[1] F_2,[2] or XeF_2,[3] More stereochemically controlled approaches utilize the epoxide opening reaction with KHF_2[4] or the displacement of 2-O-triflate by CsF.[5]

In connection with our project on the synthesis of cell surface glycans,[6] an efficient synthetic route to 2-deoxy-2-fluoro-D-mannose 8 and its glycosyl donor is required.

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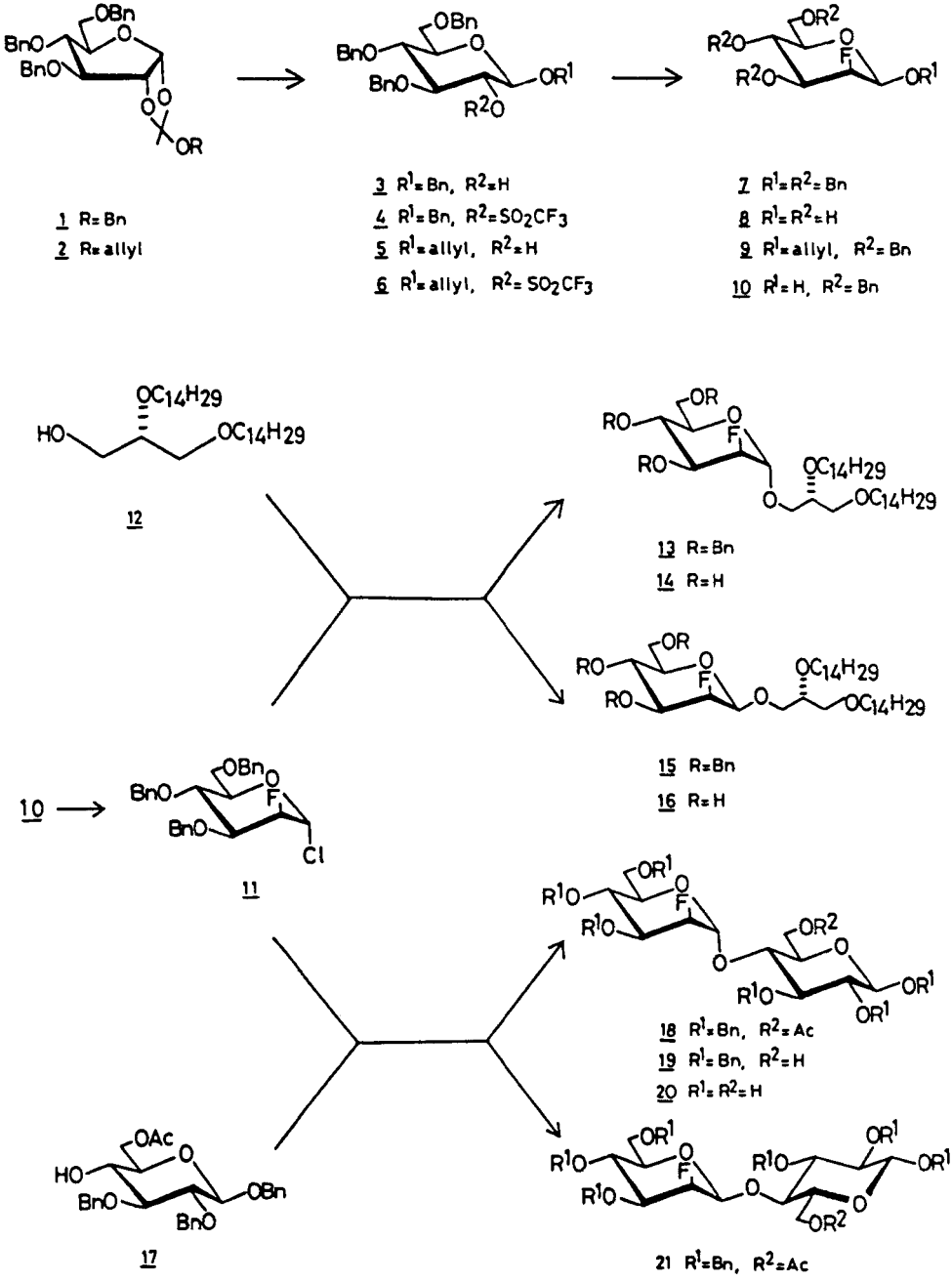

Scheme 1

We describe here, first, a stereoselective synthesis of 8, which has been reported, to the best of our knowledge, only as a minor product[7] from the addition reaction of 3,4,6-tri-O-acetyl glucal, and second, the glycosidation employing the glycosyl donor 11.

Treatment of the readily available orthoester 1 with a catalytic amount of $TMSOSO_2CF_3$[8] and powdered molecular sieves 4A, followed by deacetylation in NaOMe-MeOH afforded a 70% yield of 3, $[\alpha]_D$-23.3° *, mp 89.0-90.0° (iPr_2O). Upon treatment of 3 with $(CF_3SO_2)_2O$ in pyridine was obtained a 60% yield of 4, δ_C ($CDCl_3$): 97.96 (C-1), 84.90 (C-2). Displacement of the triflate in 4 with Bu_4NF was performed in THF at 50° to give a 77% yield of 7, $[\alpha]_D$ -48.4° , mp 70.5-71.0° (iPr_2O), δ_C ($CDCl_3$) : 97.01 (C-1, $^2J_{CF}$ 15.9 Hz), 86.90 (C-2, $^1J_{CF}$ 188.0 Hz), 80.70 (C-3, $^2J_{CF}$ 18.3 Hz). Hydrogenolysis of the benzyl groups of 7 with 10% Pd-C in AcOH afforded 8,[7] $[\alpha]_D$ +27.7° (H_2O), δ_C (D_2O, $\alpha:\beta$=2:1): 97.17 (C-1β, $^2J_{CF}$ 16.2 Hz), 91.18 (C-1α, $^2J_{CF}$ 28.4 Hz), 91.23 (C-2β, $^1J_{CF}$ 179.3 Hz), 90.26 (C-2α, $^1J_{CF}$ 170.8 Hz). δ_H (D_2O, 60°): 5.372 (H-1α, dd, $^3J_{HH}$ 1.95 Hz, $^3J_{HF}$ 7.57 Hz), 4.769 (H-2α, dt, $^2J_{HF}$ 49.1 Hz, $^3J_{HH}$ 2.20 Hz), 4.992 (H-1β, d, $^3J_{HF}$ 20.51 Hz), 4.808 (H-2β, dd, $^2J_{HF}$ 51.27 Hz, $^3J_{HH}$ 2.44 Hz).

In spite of the biochemical interests of deoxy-fluoro-oligosaccharides, there seems to be only one example for the glycosidation using 2-deoxy-2-fluorocarbohydrate reported by Vass

*Values of $[\alpha]_D$ were measured for $CHCl_3$ solution at 25°, unless noted otherwise. Compound with $[\alpha]_D$ recorded gave satisfactory data for elemental analyses.

et al.[9] In order to examine the reactivity and the selectivity of a 2-deoxy-2-fluoro-D-mannosyl donor, we prepard the glycosyl donor 11 via 9 as follows. Allyl D-glucoside 5 was readily prepared in 61% yield from 2 in the same sequence of reactions as in the preparation of 3. Trifluoromethanesulfonylation of 5 to give 6 and subsequent replacement with F^- afforded a 49% yield of 9, $[\alpha]_D$ -10.9°, δ_C ($CHCl_3$): 97.52 (C-1, $^2J_{CF}$ 14.7 Hz), 86.90 (C-2, $^1J_{CF}$ 188.0Hz, 80.59 (C-3, $^2J_{CF}$ 18.3Hz. Deallylation with $PdCl_2$-AcONa-aq.AcOH[10] to give 10 and subsequent treatment of 10 with $[Me_2N^+{=}CHOSOCl]Cl^-$ formed in situ from $SOCl_2$ and a trace of DMF in CH_2Cl_2[11] gave the glycosyl donor 11, $[\alpha]_D$ +91.8°, mp 54.0-54.5° (iPr_2O), δ_H ($CDCl_3$): 6.16 (H-1, q, $^3J_{HF}$ 7.70 Hz, $^3J_{HH}$ 3.0 Hz). In order to study the stereoselectivity of the glycosidation of 11, two glycosyl acceptors 12[12] and 17 were chosen. The glycosidation of 12 with 11 in the presence of $AgOSO_2CF_3$-powdered molecular sieves 4A in $Cl(CH_2)_2Cl$ at 20° afforded an 88% yield of a mixture of 13 and 15 in a ratio of 1:1.82. 13: $[\alpha]_D$ +38.7°, δ_C ($CDCl_3$): 97.92 (C-1, $^2J_{CF}$ 29.3 Hz). 15: $[\alpha]_D$ -2.9°, mp 48.0-48.2° (MeOH), δ_C ($CDCl_3$): 99.18 (C-1, $^2J_{CF}$ 15.9 Hz). Deprotection of 13 and 15 by catalytic hydrogen transfer in the presence of 10% Pd-C in 10:1 MeOH-HCOOH[13] afforded 14 and 16, in 89 and 88% yield, respectively. 14: $[\alpha]_D$ +28.8°, mp 62.5-64.0° (MeOH-EtOAc), δ_C ($CDCl_3$): 98.02 (C-1, $^2J_{CF}$ 29.3 Hz). δ_H ($CDCl_3$): 5.008 (H-1, dd, $^3J_{HH}$ 1.50 Hz, $^3J_{HF}$ 7.32 Hz), 4.687 (H-2, d, $^2J_{HF}$ 50.05 Hz). 16: $[\alpha]_D$ -18.4°, mp 55.0-56.0° (MeOH), δ_C ($CDCl_3$): 99.26

(C-1, $^2J_{CF}$ 14.60 Hz), δ_H ($CDCl_3$): 4.616 (H-1, d, $^3J_{HF}$ 19.29 Hz), 4.753 (H-2, dd, $^2J_{HF}$ 51.52 Hz, $^3J_{HH}$ 1.95 Hz).

The glycosidation of 17 with 11 as described above afforded a 79% yield of a mixture of 18 and 21 in a ratio of 8.72 : 1. 18: $[\alpha]_D$+15.3° , mp 118.5-119.0° (iPr_2O), δ_C ($CDCl_3$): 102.0 (C-1a), 99.64 (C-1b, $^2J_{CF}$ 29.3 Hz). 21: $[\alpha]_D$ +8.3° , mp 117.5-119.0° (EtOAc-iPr_2O), δ_C ($CDCl_3$): 102.4 (C-1a), 98.31 (C-1b, $^2J_{CF}$ 15.9 Hz). Deacetylation of 18 to give 19 and subsequent deprotection of 19 by catalytic hydrogen transfer[13] afforded 20, $[\alpha]_D$ +100.0° (H_2O), δ_C (D^2O, α : β = 1 : 2): 98.73 (C-1bα, $^2J_{CF}$ 29.7 Hz), 98.64 (C-1bβ, $^2J_{CF}$ 29.7 Hz), 96.18 (C-1aβ), 92.24 (C-1aα). δ_H (D_2O, 60°): 5.481 (C-1b$\alpha\beta$, $^3J_{HF}$ 7.81 Hz, $^3J_{HH}$ 1.71 Hz), 5.233 (H-1aα, $^3J_{HH}$ 3.7 Hz), 4.631 (H-1aβ, $^3J_{HH}$ 8.1 Hz). The obseved $^2J_{C-1,F}$ values for the synthetic samples, 14.7-16.2 Hz for β-D-manno and 28.4-29.7 Hz for α-D-manno, were in good agreement with the reported values[14] of 15.8 and 29.6 Hz, respectively. And also the observed $^3J_{H-1,F}$ values 19.29-20.51 Hz and 7.32-7.81 Hz for the synthetic samples were in good agreement with the reported values[15] of 20.0 and 7.5 Hz for β-D-manno and α-D-manno configurations, respectively.

In conclusion, an efficient approach to the stereoselective synthesis of 2-deoxy-2-fluoro-D-mannose 8 and the glycosyl donor 11 is developed, and the preferred α-D-stereoselectivity in the glycosidation of 11 with a less reactive aglycon is demonstrated in accordance with the general trend[16] in the glycoside synthesis.

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