Carbohydrate Research 343 (2008) 2992–2996

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Note

Synthesis of fructofuranosides: efficient glycosylation with *N*-phenyltrifluoroacetimidate as the leaving group

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ARTICLE INFO

Article history:
Received 19 May 2008
Received in revised form 27 August 2008
Accepted 1 September 2008
Available online 9 September 2008

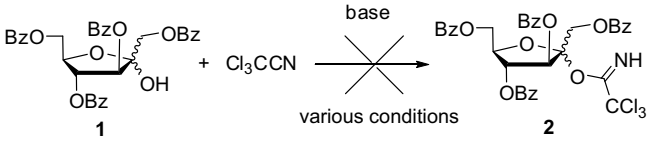
Dedicated to Professor Yongzheng Hui on the occasion of his 70th birthday

Keywords:
Fructosylation
Trifluoroacetimidate
Glycosyl donor

ABSTRACT

Fructofuranosyl trifluoroacetimidate **3** was demonstrated to be an effective glycosyl donor that exhibited good α-selectivity and good yield in fructosylation reactions. The reaction proceeds via neighboring group participation, which was proved by the isolation of a stable allylic orthoester intermediate.

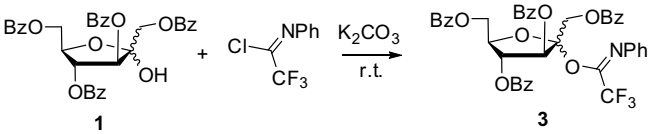
Fructose is the second most abundant simple sugar (behind glucose) in nature, and fructosides are found abundantly in both plants and bacteria. Fructose-containing molecules are not only storage materials, but are also involved in a wide range of biological processes.[1] However, the chemical synthesis of fructosides has lagged far behind that of glucosides. The major impediment is that fructosylation protocols with good stereoselectivity and good yield are limited.[2–4] Generally, D-fructose occurs as β-furanosyl residues, but fructosylation methods with β-selectivity are particularly limited.[3] There are two major fructosylation protocols. One is the thiofructoside glycosylation, developed by Oscarson et al.,[2a] which led ultimately to the first stereospecific synthesis of sucrose, which contains a β-fructofuranoside moiety, in 2000.[3] This protocol is β-stereoselective, but the donor required is costly to prepare, which limits its synthetic application. The other method uses fructosyl phosphite donors, with which good yields were obtained but the stereochemical outcome was not predictable.[4] We note that the Schmidt glycosylation protocol using trichloroacetimidate as leaving group is not suitable for fructosylation, because fructosyl trichloroacetimidate **2** could not be prepared under various basic conditions (Scheme 1).[4,5] To reach the goal of efficient and stereoselective β-fructosylation, the development of new and effective fructosylation methods are necessary.



Scheme 1.

Yu et al. recently developed an alternative donor to the trichloroacetimidate, *N*-phenyl trifluoroacetimidate,[6] which was successfully applied in direct sialylation,[7] N-glycosylation of primary amides,[8] O-glycosylation of hydroxamic acid,[9] and several total synthesis.[10] These results stimulated our interests to apply this class of donors in fructosylation. Our preliminary work in this area is reported here.

Initially, we investigated the preparation of trifluoroacetimidate **3** (Scheme 2 and Table 1). 1,3,4,6-Tetra-*O*-benzoylfructose **1**, which was readily prepared from D-fructose,[11] was treated with



Scheme 2.

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doi:10.1016/j.carres.2008.09.001

Table 1
Optimization of the preparation of *N*-phenyl trifluoroacetimidate **3**

Entry	*N*-phenyl trifluoroacetimidoyl chloride (equiv)	Solvent	Reaction time (h)	Yield (%)
1	7	Anhydrous CH_2Cl_2	20	10
2	7	'Wet' CH_2Cl_2	4	70
3	3	Acetone	2	Quant.

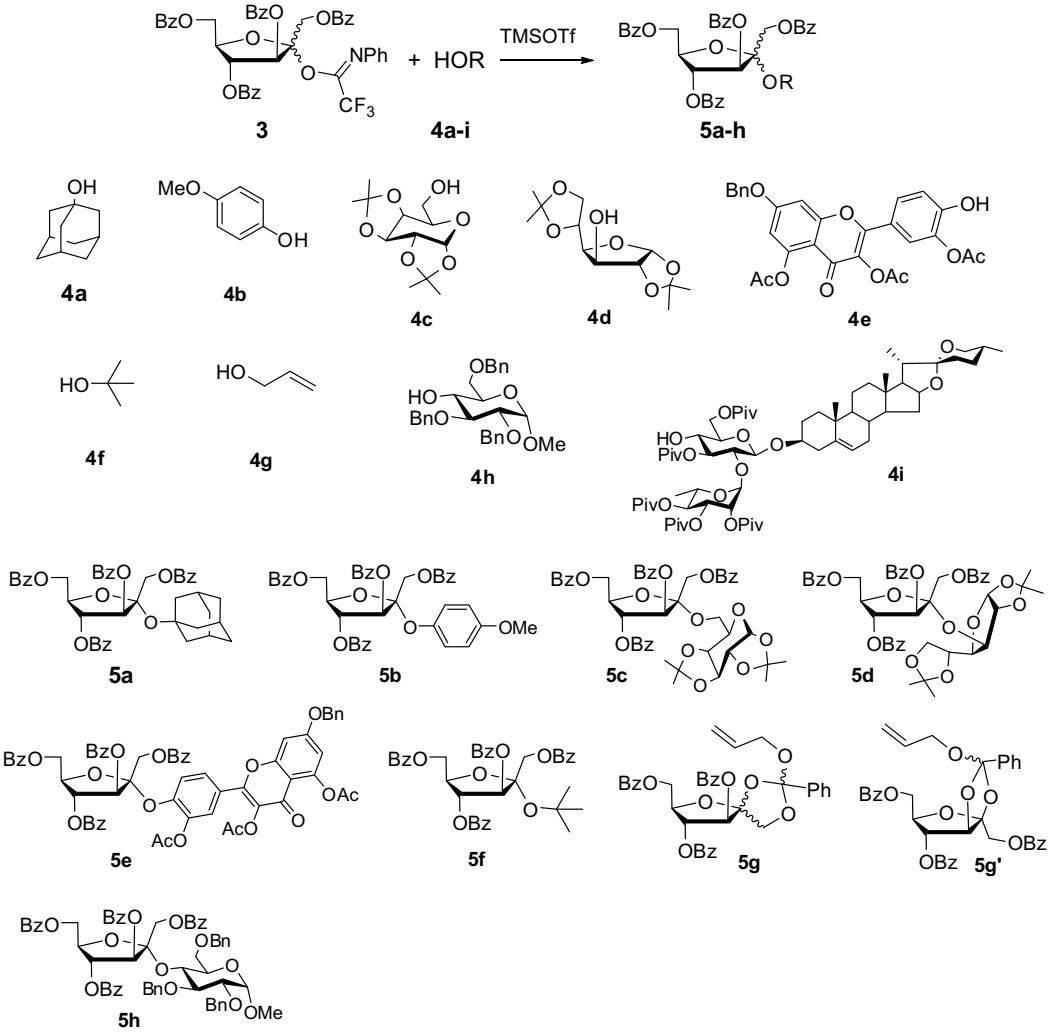
N-phenyltrifluoroacetimidoyl chloride (7 equiv) in the presence of K_2CO_3 (3 equiv) in anhydrous CH_2Cl_2 at room temperature overnight to provide the donor **3**, in only 10% yield.[12] However, when CH_2Cl_2 without drying pretreatment was used, the donor **3** was obtained in 70% yield in 4 h. These results indicated that a little moisture benefits the reaction. Further optimization showed a better result: The donor **3** was obtained in quantitative yield in 2 h, with acetone as solvent, and only 3 equiv of *N*-phenyltrifluoroacetimidoyl chloride was needed. Fructosyl imidate **3** was purified by silica gel column chromatography and was stable in storage at 4 °C for at least five weeks. The facile preparation and stability of **3** bode well for its possible advantages for applications in the synthesis of fructofuranosides.

The donor properties of **3** were first examined with admantanol **4a** as the acceptor (Scheme 3). To a stirring mixture of **3**, **4a** and 4 Å MS in CH_2Cl_2 at −20 °C under argon, TMSOTf (0.06 equiv) was added slowly. After 2 h, the promotor was quenched with Et_3N. Usual workup provided admantanyl α-fructofuranoside **5a** stereoselectively in 97% yield (Table 2, entry 1). Replacement of CH_2Cl_2 with CH_3CN as solvent also afforded **5a** in 92% yield (entry 2).

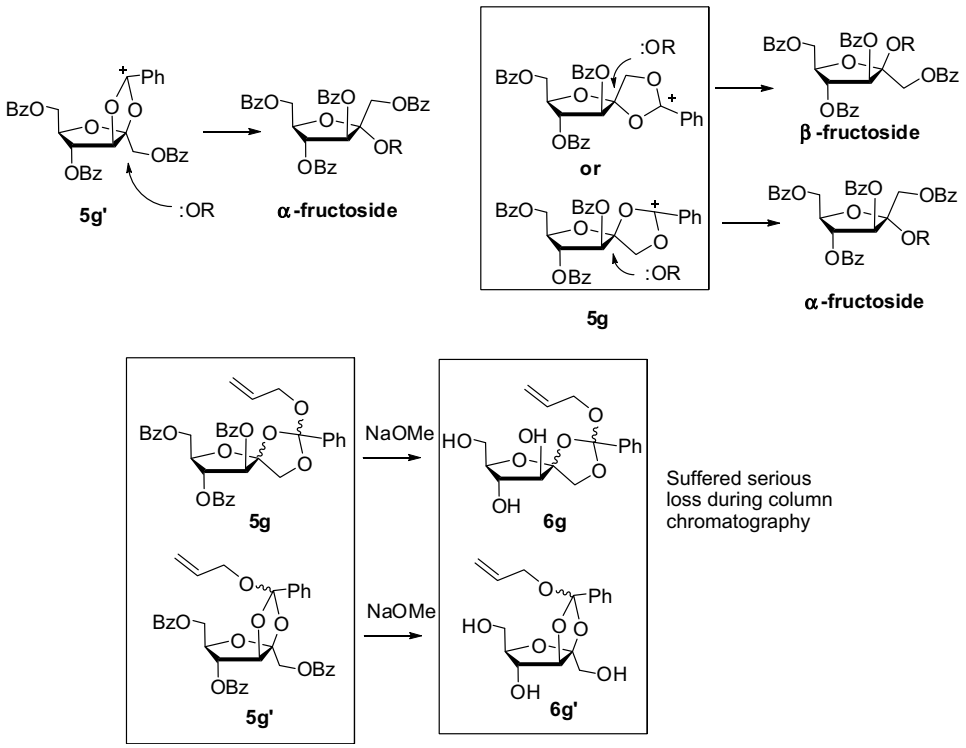
Table 2
Glycosylation with tetrabenzoyl *N*-phenyl trifluoroacetimidate **3** as donor

Entry	Acceptor	Conditions	Product	Yield[d] (%)	α:β
1	**4a**	A[a]	**5a**	97	α Only
2	**4a**	B[b]	**5a**	92	α Only
3	**4b**	A	**5b**	97	α Only
4	**4c**	A	**5c**	96	α Only
5	**4d**	A	—	No product	
6	**4d**	B	—	No product	—
7	**4d**	C[c]	**5d**	63	α Mainly
8	**4e**	A	**5e**	57[e]	α:β = 5:2[f]
9	**4f**	A	**5f**	70	α Only
10	**4g**	C	**5g** or **5g′**	63	—
11	**4h**	A	**5h**	63	α Only
12	**4i**	A	No reaction	—	—

[a] A: −20 °C, 0.06 equiv TMSOTf, CH_2Cl_2, then rt 1 h.
[b] B: −20 °C, 0.06 equiv TMSOTf, CH_3CN, then rt 1 h.
[c] C: −20 °C, 0.06 equiv TMSOTf, CH_2Cl_2, then 0 °C, additional 0.06 equiv TMSOTf, rt 1 h.
[d] Isolated yield.
[e] Isolated yield for the α-anomer.
[f] The ratio was determined by HPLC.



Scheme 3. Acceptor substrates (**4**) and products (**5**) in fructosylation reactions.



Scheme 4.

Although acetonitrile was reported to improve the β-glycosylation selectivity;[13] here there was no solvent effect. The anomeric configuration of the fructofuranosides was assigned by the characteristic C-2 signals in the ^{13}C NMR spectra. C-2 resonances at higher field, around 103–105 ppm, were assigned as β-fructofuranosides, and C-2 signals at lower field, around 107–109 ppm, were assigned as α-linkages.[2]

Thus, the optimized glycosylation conditions were applied to other acceptors (**4b**–**i**). For most of the acceptors, the α-fructofuranosides were obtained in fair to excellent yields (Table 2). This glycosylation method worked well with several other kinds of acceptors, including primary and secondary hydroxyl glycosyl acceptors (entries 4, 7, and 11), phenolic or tertiary alcohols (entries 1, 3, and 9), and flavones (entry 8). For acceptors **4a**–**4c**, **4f** and **4h**, the α-fructofuranosides were obtained stereoselectively, all in moderate to good yield. For the 4-hydroxy acceptor **4h**, only the α-anomer was obtained in 63% yield (entry 11) while β-selectivity was reported by Schmidt when phosphite donor was used.[4] For **4d**, when 0.06 equiv of TMSOTf was used, none of the desired product was obtained; instead a compound, which was proposed to be the orthoester by-product (**5g**/**5g**′ entries 5 and 6) was obtained. With more 0.06 equiv TMSOTf, the α-fructoside was obtained as main product in 63% yield (entry 7).[14] It is noteworthy that for this kind of highly hindered acceptor, no successful glycosylation of ketoses have been reported previously, thus demonstrating the remarkable donor properties of **3**. However, for acceptor **4i**, which has great steric hindrance, glycosylation did not occur (entry 12). For the fructosylation of flavone **4e**, a mixture of fructofuranosides (α:β = 5:2, by HPLC) was obtained, with the α-anomer being isolated in 57% yield (entry 8). This reaction represents the first fructosylation of a flavone.

Interestingly, when allylic alcohol was used, an orthoester was obtained in 63% yield (entry 10), which provided the evidence that the glycosylation reaction proceeds through the neighboring group participation (NGP) pathway. The formation of orthoester was confirmed by ^{1}H and ^{13}C NMR spectroscopy (123.03 ppm, quaternary carbon of orthoester). The orthoester was further debenzoylated with sodium methoxide to determine the exact NGP pattern[15†] (Scheme 4). Unfortunately, due to the lability of deacylated orthoester to weak acidic conditions, the product **6g** (or **6g**′) suffered serious loss during silica gel column chromatography with CH_2Cl_2–MeOH as eluent. Although the exact NGP pattern was not resolved, the isolated orthoester provided valuable mechanism information, helping to explain the stereoselectivity of the glycosylation. Participation of the acyl group on O-3 would result in exclusive α-selectivity, and participation by the acyl group on O-1 suggests a possible pathway for β-fructosylation (Scheme 4).

In conclusion, fructofuranosyl trifluoroacetimidate **3** exhibits good glycosyl donor properties, with the α-fructosylation of flavone **4e** and the highly hindered secondary hydroxyl acceptor **4d** being reported for the first time. The glycosylation, which shows good α-selectivity, likely proceeds through an NGP pathway, which was proven by the isolation of a stable allylic orthoester intermediate. Although the β-fructoside, which is of more biological interest and more difficult to synthesize, could not be obtained in good yields with the tetrabenzoyl donor **3**, the successful application of *N*-phenyl trifluoroacetimidate donors to this problem provides a new protocol to the limited number of fructosylation methods. Further application studies are ongoing in our laboratory.

1. Experimental

1.1. General methods

Solvents were purified in the usual way. Thin layer chromatography (TLC) was performed on precoated plates of Silica Gel

† The orthoester structure is stable under basic conditions. Treatment of **5g** (**5g**′) with NaOMe produced **6g** or **6g**′. For **6g**, compared with **5g**, the H-3 signal will be shifted upfield and the two H-1 signals will remain unchanged; and for **6g**′, compared with **5g**′, the two H-1 signals will shift upfield and the H-3 signal will remain unchanged. By comparison of the ^{1}H NMR data of the deacylated product and **5g** (**5g**′), the structure of the intermediate can be determined.

HF254 (0.5 mm, Yantai, China). Flash column chromatography was performed on Silica Gel H (10–40 μm, Yantai, China). Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter. IR spectra were recorded on a NICOLET FTIR-360 spectrometer. NMR spectra were recorded on a Bruker AM 300 spectrometer with Me_4Si as the internal standard. Mass spectra were recorded on a HP5989A or a VG Quatro mass spectrometer. Elemental analyses were recorded on a Perkin–Elmer Model 2400 instrument.

1.2. 1,3,4,6-Tetra-*O*-benzoyl-α,β-D-fructofuranosyl-2-(*N*-phenyl)-trifluoroacetimidate (3)

To fructoside **1** (594 mg, 1.0 mmol) and **2** (0.45 mL, 3 mmol) in acetone (AR grade, 8 mL) was added K_2CO_3 (410 mg, 3 mmol), and the mixture was stirred at rt for 2 h. The mixture was filtered, concentrated, and the residue was purified by column chromatography (hexane–EtOAc 7:1) to obtain **3** (691 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04–7.07 (m, 22H, Ar), 7.07 (t, 1H, *J* 7.5 Hz, NPh–H), 6.73 (d, 2H, *J* 7.5 Hz, NPh–H), 6.29 (d, 1H, *J* 6.6 Hz), 6.12 (t, 1H, *J* 6.0 Hz), 5.27 (d, 1H, *J* 11.7 Hz), 4.97 (d, 1H, *J* 12.0 Hz), 4.83–4.73 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.94, 165.59, 165.30, 164.99, 143.07, 141.28 (ddd, *C*=NPh), 131.90–128.23 (Ar), 119.25, 115.72 (ddd, *C*F_3), 106.89, 80.58, 77.32, 76.61, 64.24, 63.95. Anal. Calcd for $C_{42}H_{52}F_3NO_{10}$: C, 65.71; H, 4.20; N, 1.82. Found: C, 65.94; H, 4.35; N, 1.75. ESI-MS (*m*/*z*): 790.5 ($M+Na^+$).

1.3. Typical procedure for the coupling of fructosyl *N*-phenyltrifluoroacetimidate with alcohols

A mixture of the fructosyl trifluoroacetimidate **3** (100 mg, 0.13 mmol), alcohol (0.2 mmol, 1.5 equiv), and 4 Å MS (150 mg) in anhydrous CH_2Cl_2 (2 mL) was stirred at −20 °C for 30 min under Ar. TMSOTf in CH_2Cl_2 (0.06 equiv, 0.09 mL, 0.09 M) was added dropwise. After stirring for 1.5 h, the mixture was warmed to rt and the reaction was monitored by TLC. When complete, the solution was neutralized by Et_3N (0.5 mL), and the resulting mixture was filtered through Celite. The filtrates were concentrated and purified by column chromatography to obtain the fructoside.

1.4. Adamantan-1-yl 1,3,4,6-tetra-*O*-benzoyl-α-D-fructofuranoside (5a)

Yield: 97%. $[\alpha]_D^{25}$ +11.0 (*c* 1.0, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13–7.22 (20H, Ar), 5.87 (d, 1H, *J* 1.6 Hz), 5.50 (dd, 1H, *J* 4.1 Hz), 4.82–4.63 (m, 5H), 2.11 (s, 3H), 2.0 (br s, 6H), 1.61 (br s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 165.8, 165.7, 164.7, 133.4–128.2, 108.0, 82.8, 81.3, 78.6, 77.2, 64.0, 63.5, 44.3, 36.1, 30.9. ESIMS *m*/*z* calcd for $C_{44}H_{42}O_{10}Na$: 753.27. Found: 753.35. Anal. Calcd for $C_{44}H_{42}O_{10}$: C, 72.31; H, 5.79. Found: C, 72.20; H, 5.76. IR (cm^{-1}) ν_{max} = 2910, 1725, 1273, 1112, 709.

1.5. 4′-Methoxyphenyl 1,3,4,6-tetra-*O*-benzoyl-α-D-fructofuranoside (5b)

Yield: 97%. $[\alpha]_D^{25}$ −30.6 (*c* 0. 5, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14–7.25 (m, 20H), 7.12 (d, 2H, MP-H), 6.80 (d, 2H, MP-H), 6.21 (t, 1H, *J* 1.5 Hz), 5.68 (dd, 1H, *J* 4.8, 1.8 Hz), 4.89–4.76 (m, 3H), 4.58 (s, 2H), 3.76 (s, 3H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 165.9, 165.6, 164.8, 156.2, 146.5, 133.4–128.1, 123.1, 115.9, 114.4, 109.0, 81.4, 78.3, 63.5, 60.6, 55.5, 55.2. ESIMS *m*/*z* calcd for $C_{41}H_{34}O_{11}Na$: 725.1993. Found: 725.1998. IR (cm^{-1}) ν_{max} = 1728, 1511, 1273, 1236, 1029, 711.

1.6. 1,3,4,6-Tetra-*O*-benzoyl-α-fructofuranosyl-(2→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (5c)

Yield: 96%. $[\alpha]_D^{25}$ −0.4 (*c* 1.1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20–7.23 (20H, Ar), 5.92 (d, 1H, *J* 1.2 Hz), 5.55 (dd, 1H, *J* 4.5 Hz), 5.51 (d, 1H, *J* 5.1 Hz), 4.97 and 4.40 (AB, 2H, *J* 12.0 Hz), 4.86 (dd, 1H, *J* 11.4 Hz), 4.74–4.67 (m, 2H), 4.54 (dd, 1H, *J* 8.1 Hz), 4.31–4.25 (m, 2H), 4.0 (td, 1H), 3.91–3.84 (m, 2H), 1.38, 1.37, 1.30, 1.13 (all s, 3H each, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 165.8, 165.5, 164.7, 133.4–128.2, 109.2, 108.4, 107.2, 96.3 (C-1), 81.4, 81.0, 78.9, 71.0, 70.6, 70.4, 66.9, 63.6, 60.6, 59.5, 25.9, 25.8, 24.9, 24.2. ESIMS *m*/*z* calcd for $C_{46}H_{46}O_{15}Na$, 861.27. Found: 861.45. IR (cm^{-1}) *ν* 2983, 1720, 1270, 1067, 706. Anal. Calcd for $C_{46}H_{46}O_{15}$: C, 65.86; H, 5.53. Found: C, 65.92; H, 5.71.

1.7. 1,3,4,6-Tetra-*O*-benzoyl-α-D-fructofuranosyl-(2→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside (5d)

Yield: 63%. $[\alpha]_D^{25}$ −4.1 (*c* 1.0, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12–7.21 (20H, Ar), 6.03 (d, 1H, *J* 1 Hz), 5.81 (d, 1H, *J* 3.6 Hz), 5.54 (br s, 1H), 4.82–4.67 (m, 5H), 4.57–4.50 (m, 2H), 4.35 (m, 1H), 4.14–4.01 (m, 2H), 3.87 (m, 1H), 1.47, 1.31, 1.14, 0.86 (all s, 3H each, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 165.5 (2C), 164.5, 133.9–128.3, 112.0, 109.2, 109.1, 105.0 (C-1), 84.0, 83.4, 80.9, 80.5, 78.6, 75.2, 71.8, 66.9, 63.9, 61.5, 27.0, 26.7, 26.1, 24.6. ESIMS *m*/*z* calcd for $C_{46}H_{46}O_{15}Na$, 861.27. Found: 861.45. IR (cm^{-1}) *ν* 2988, 1728, 1273, 1071, 709. Anal. Calcd for $C_{46}H_{46}O_{15}$: C, 65.86; H, 5.53. Found: C, 65.89; H, 5.76.

1.8. 3,5,3′-Triacetyl-7-benzylquercetin-4′-yl-1,3,4,6-tetra-*O*-benzoyl-α-D-fructofuranoside (5e)

α-Anomer was purified by preparative TLC (R_f = 0.28, toluene–EtOAc 8:1) Yield: 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14–7.78 (9 H, m, Ar), 7.70–7.26 (19H, m, Ar), 6.91 (d, 1H), 6.72 (m, 1H), 6.16 (d, 1H), 5.74 (d, 1H), 5.16 (s, 2H), 4.89–4.86 (m, 3H), 4.76–4.68 (m, 2H), 2.45 (s, 3H), 2.31 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 169.5, 168.3, 168.0, 166.0, 165.6, 165.2, 164.6, 162.7, 158.0, 153.4, 150.6, 147.5, 142.2, 135.1, 133.7–126.8 (m, Ar), 125.3, 123.5, 120.5, 111.1, 110.4, 109.2, 99.7, 81.9, 81.8, 70.7, 63.1, 60.3, 60.1, 21.1, 21.0, 20.5, 20.4. ESIMS *m*/*z* calcd for $C_{62}H_{48}O_{19}Na$: 1119.29. Found: 1119.60.

1.9. *t*-Butyl 1,3,4,6-tetra-*O*-benzoyl-α-D-fructofuranoside (5f)

Yield: 70%. $[\alpha]_D^{26}$ +16.8 (*c* 1.1, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15–7.22 (20H, Ar), 5.88 (d, 1H, *J* 0.9 Hz), 5.49 (d, 1H, *J* 2.7 Hz), 4.86–4.60 (m, 5H), 1.43 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 165.8, 165.7, 164.7, 133.4–128.3, 108.1, 82.7, 81.5, 78.7, 64.1, 62.9, 60.3, 30.7. ESIMS *m*/*z* calcd for $C_{38}H_{36}O_{10}Na$: 675.2206. Found 675.2207. IR (cm^{-1}) ν_{max} = 2979, 1725, 1273, 1113, 710.

1.10. Methyl 1,3,4,6-tetra-*O*-benzoyl-α-D-fructofuranosyl-(2→4)-2,3,6-tri-*O*-benzyl-α-D-glucofuranoside (5h)

Yield: 63%. $[\alpha]_D^{26}$ −11.8 (*c* 1.5, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15–7.09 (35H, Ar), 6.01 (d, 1H, *J* 5.4 Hz), 5.70 (dd, 1H, *J* 5.4, 6.3 Hz), 4.94–3.56 (m, 18H), 3.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 165.5, 165.4, 164.9, 138.2–125.3, 107.6, 97.6, 82.3, 80.3, 80.1, 78.5, 76.8, 75.8, 73.4, 73.1, 72.9, 70.2, 69.3, 64.1, 63.0, 55.1. ESIMS *m*/*z* calcd for $C_{62}H_{58}O_{15}Na$: 1065.3673. Found: 1065.3668. IR (cm^{-1}) ν_{max} = 2918, 1729, 1272, 1097, 710.

1.11. Allylic orthoester derived from glycosylation of allyl alcohol with 1,3,4,6-tetra-*O*-benzoyl-α,β-D-fructofuranosyl-2-(*N*-phenyl)-trifluoroacetimidate (5g or 5g′)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06–7.24 (m, 20H, Ar), 5.78 (m, 1H), 5.53 (d, 1H), 5.23–5.07 (m, 3H), 4.93–4.69 (m, 3H), 4.37–4.23 (m, 2H), 3.89 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 165.9, 165.5, 135.2, 133.5–126.4, 123.0, 116.8, 114.3, 85.7, 84.9, 78.3, 65.0, 64.5, 63.9.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (29925203) and the Committee of Science and Technology of Shanghai (02QMA1401). F.L. thanks the Open Foundation of State Key Lab of Biochemistry and Natural Products Chemistry, SIOC.

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