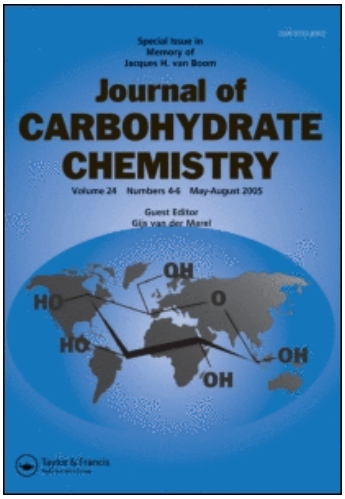

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REACTION OF SUGAR PHOSPHONATES WITH SUCROSE ALDEHYDES. SYNTHESIS OF HIGHER ANALOGS OF SUCROSE

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Dedicated to Professor Gerard Descotes on the occasion of his 68th birthday and for his great achievements in sugar chemistry.

ABSTRACT

The Horner-Emmons reaction between sugar phosphonates Sug-C(O)CH_2 P(O)$(OMe)_2$ and aldehydes derived from sucrose afforded precursors of higher analogs of the general formula Sug-C(O)CH═CH-Suc. An example of the functionalization of the internal three-carbon saccharide connecting unit is provided.

INTRODUCTION

Recently we elaborated a convenient methodology for the preparation of sucrose derivatives having either terminal OH free (at positions C-1′, C-6 and C-6′; compounds **1**, **2**, and **3**, respectively) and in which all secondary hydroxyl groups were protected as − easily removable under neutral conditions—benzyl ethers.[1]

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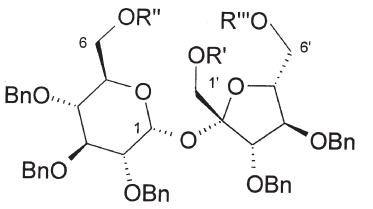

1 R' = H, R'' = R''' = *p*-$O_2NC_6H_4C(O)$-
2 R' = BOM, R'' = H, R''' = TBDPS
3 R' = BOM, R'' = TBDPS, R''' = H

Oxidation of either terminal free hydroxyl group to an aldehyde, followed by reaction with the simplest stabilized ylid ($Ph_3P{=}CHCO_2Me$) and osmylation of the resulting α,β-unsaturated ester, led to higher sucrose analogs elongated by two carbon atoms.[1] This approach might be regarded as an application of a Brimacombe methodology[2] to sucrose chemistry. We reasoned that availability of the different sucrose aldehydes should also open a convenient route to even higher derivatives by coupling of sucrose with different monosaccharide sub-units.

RESULTS AND DISCUSSION

Our strategy for the preparation of the sucrose analogs consisted of three major steps: *i.* coupling of sucrose ('Suc'CH_2OH) with simple monosaccharide ('Sug'CH_2OH) moieties via an additional carbon ('C_1') atom, *ii.* functionalization of the resulting allylic bridge and *iii.* final deprotection (Fig.1).

The Horner-Emmons methodology was particularly useful for the construction of a higher sugar skeleton from simple monosaccharides,[3,4] and so we decided, therefore, to apply this reaction to the synthesis of higher analogs of sucrose.

Synthesis of the Higher Sucrose Precursors

The phosphonates **4**,[4] **5**,[5] **6**,[4] and **7**[6] used in this study, derived from 1,2:3,4-di-*O*-isopropylidene-*α*-D-galactose, benzyl *α*-D-mannoside, L-*threo*-β-D-*gluco*-octose and sucrose, respectively, were prepared conveniently by reaction of the corresponding methyl uronates with dimethyl methyl phosphonate anion (Fig. 2).

To check the applicability of the Horner-Emmons methodology in sucrose chemistry we performed the coupling of all three sucrose aldehydes (**1a**, **2a**, and

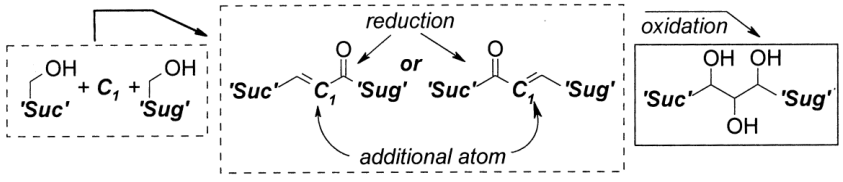

Figure 1. Synthetic plan for the preparation of higher analogs of sucrose.

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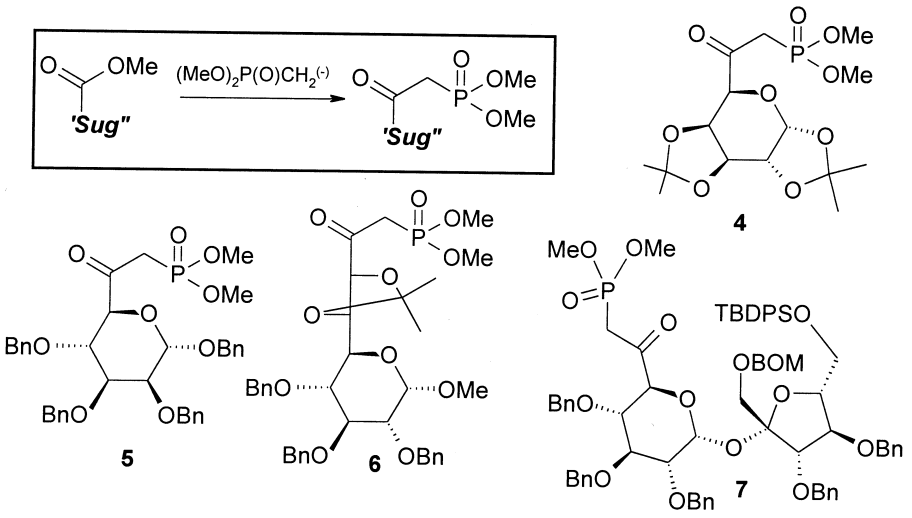
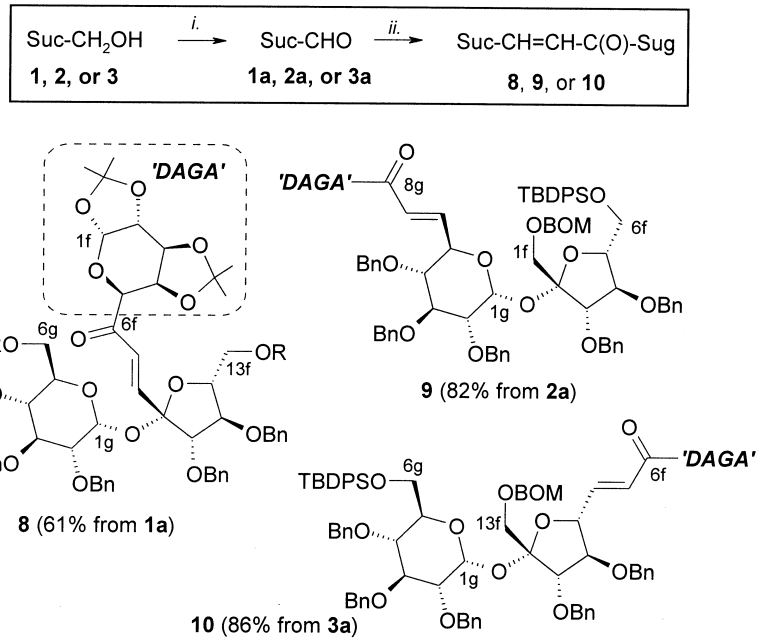


Figure 2. Preparation of sugar phosphonates.

3a; see Scheme 1) with one selected phosphorous reagent, dimethyl (1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-heptopyranos-6-ulos-7-yl)phosphonate (**4**).

Under the mild phase-transfer conditions (K_2CO_3, 18-crown-6, toluene, room temp) phosphonate **4** reacted with the corresponding regioisomeric aldehydes **1a–3a** to afford all three sucrose derivatives homologated by 7-carbon atoms at the C-1′- (**8**, 61%), C-6 (**9**, 82%) and C-6′ (**10**, 86%) positions (Scheme 1). The con-



Scheme 1. *i.* $(COCl)_2$, DMSO, Et_3N; *ii.* **4**, K_2CO_3, 18 = crown = 6, toluene, rt.

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figuration of the newly created double bonds in all these compounds were assigned as *E* on the basis of the ^{1}H NMR data ($J_{olef.}$ ~16 Hz). Enone **8**, homologated at the C-1′, was obtained in relatively lower yield, since this *neo*-pentyl-like position is much less reactive than C-6 and C-6′.

Having established the usefulness of the phosphonate method for the preparation of regioisomeric sucrose enones, we concentrated our attention on the extension of this reaction to other phosphonates.

Phosphonates **5** and **6** reacted with aldehyde **2a** (derived from alcohol **2**) under the same mild phase-transfer conditions affording the corresponding higher sucrose enones **11** and **12** in good yields. Moreover, compound **13**, regioisomeric to enone **9**, was readily prepared by reaction of sucrose phosphonate **7** and 'diacetonogalactose' aldehyde.

The enones obtained in this study, together with the previously prepared[1] compound **14**, represent a wide variety of such modified sucroses (Fig. 3) and are good evidence of the usefulness of the phosphonate methodology in sucrose chemistry.

Functionalization of Selected Higher Sucrose Enone

The next problem to be solved in the synthesis of higher sucrose derivatives was the functionalization of the allylic bridge connecting the sucrose and the monosaccharide units. Consequently, we decided to apply a general methodology we described over the past several years for the transformation of a higher sugar

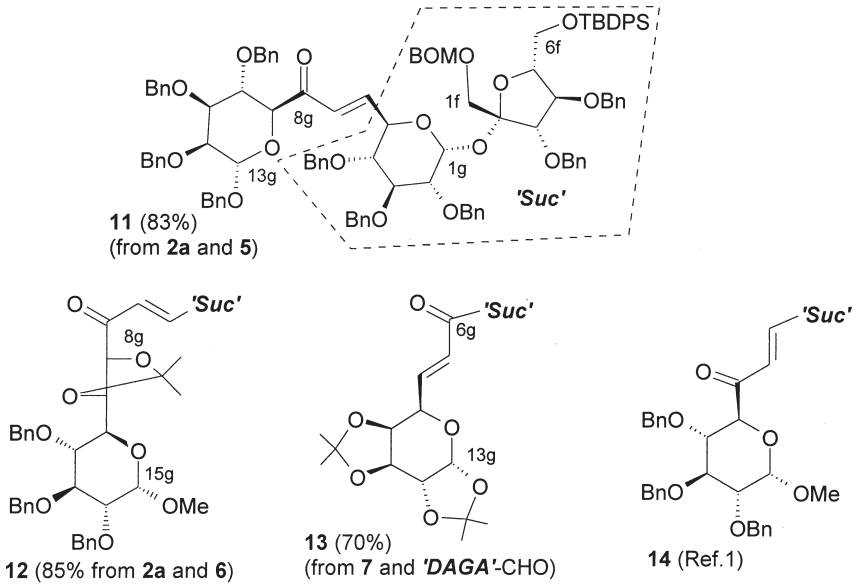


Figure 3. Different higher sucrose enones prepared by a phosphonate method.

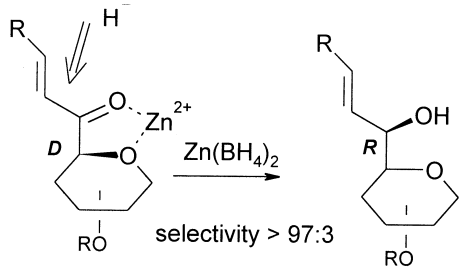


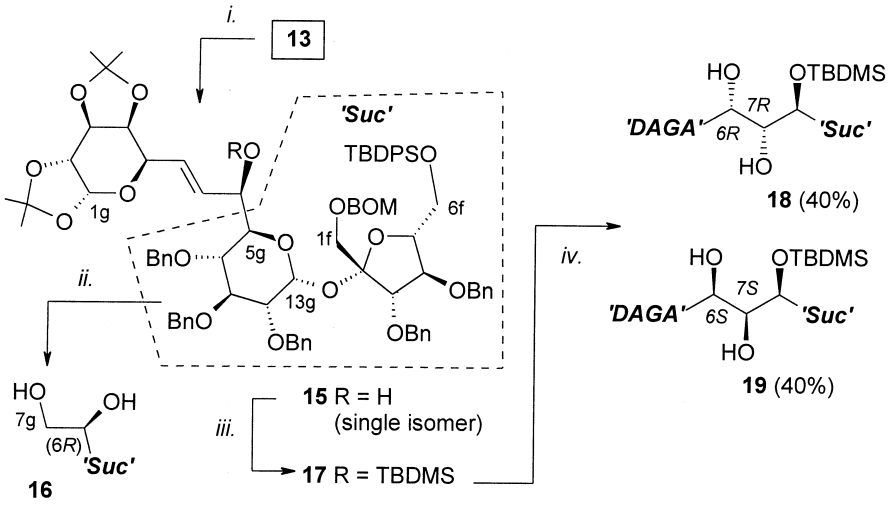
Figure 4. Stereochemistry of the reduction of higher monosaccharide enones of the D-series with zinc borohydride[7].

enone system into a triol moiety. Reduction[7] of the carbonyl function of the 2-unsaturated ketone in such enones (D-series) can be performed with high stereoselectively using zinc borohydride (Fig. 4).

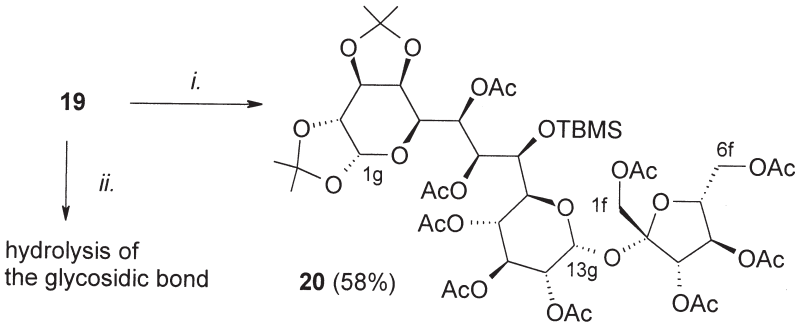
The residual carbon to carbon double bond of the allylic alcohol unit might then be oxidized conveniently with osmium tetraoxide to the corresponding triol.[8] We expected that the above-presented methodology might be also successfully applied in a functionalization of higher sucrose enones.

Indeed, treatment of the enone **13** with $Zn(BH_4)_2$ afforded exclusively allylic alcohol **15** (Scheme 2) in which the *R*-configuration at the newly created chiral center was assigned on the basis of the CD spectral data.[1,9] The positive Cotton effect (at λ 306 nm) observed for a complex of **16** (obtained in two simple steps from **15**) with dimolybdenum tetraacetate pointed unequivocally to an *R*-configuration at the C-6 position.

Dihydroxylation of a double bond in allylic alcohol **15** would afford a triol, in which determination of the configuration at the newly created chiral centers



Scheme 2. *i.* $Zn(BH_4)_2$, Et_2O, 0 °C, 83%; *ii. a).* O_3, CH_2Cl_2-MeOH, −78 °C; *b).* $NaBH_4$, 68%; *iii.* TBMSCI, DMAP, imidazole, DMF, 90 °C, 88%; *iv.* OsO_4 (cat.), NMO.



Scheme 3. *i. a)* Na/NH_3, -78 °C, 30 min; *b)* Ac_2O, Py; *ii.* H_2/Pd/C, AcOH (cat).

might be difficult. We decided, therefore, to protect the free hydroxy group as a *tert*-butyldimethylsilyl ether (→ **17**), since the configuration of the resulting *threo*-diol might be readily determined by CD spectroscopy. Moreover, such protection should not affect the selectivity of the osmylation resulting from Kishi's rule.[10]

Catalytic osmylation of the double bond in compound **17** afforded, however, both stereoisomeric diols **18** and **19** in a 1:1 ratio (Scheme 2), although both oxygen functions flanking the double bond should act in the same direction. This observation confirmed our earlier findings[1] that such a dihydroxylation is much less selective in sucrose chemistry than in similar transformations of higher monosaccharides.

Determination of the configuration at the newly created chiral centers in **18** and **19** was based on the CD spectra of the complexes of both diols with dimolybdenum tetraacetate. The positive Cotton effect at $\lambda = 304.5$ nm recorded for a complex of **18** pointed to the 6*R*,7*R* configurations while the negative effect at $\lambda = 321.5$ nm for a complex of **19** proved the 6*S*,7*S* geometry at these stereogenic centers.

The final step in our synthesis of higher sucrose derivatives was deprotection of the protected sucrose unit. Hydrogenolysis over palladium on charcoal did not remove the benzyl groups, while the same reaction performed in the presence of small amounts of acetic acid resulted in hydrolysis of the glycosidic linkage. However, the benzyl groups, the BOM and TBDPS groups, but not TBDMS group, were removed with sodium in liquid ammonia. Acetylation of the crude product afforded the final compound **20** in 58% overall yield.

CONCLUSIONS

The sucrose molecule was conveniently homologated at either terminal position by a Horner-Emmons reaction of the corresponding sugar phosphonates with aldehydes derived from sucrose, affording enones of general formula Suc-CH═CH-C(O)-Sug. An alternative version, reaction of the sucrose phosphonate with a sugar aldehyde was also possible. The three-carbon-atom bridge in each

enone was converted into a triol system by highly stereoselective reduction of the carbonyl function with zinc borohydride, followed by *cis*-dihydroxylation of the double bond. The latter process was completely non-selective (a 1:1 ratio of isomeric diols was obtained) in agreement with our earlier observation on the very low selectivity of osmylation of sucrose derivatives.

The benzyl and benzyloxymethyl alcohol protecting groups on the sucrose backbone could not be removed by catalytic hydrogenolysis, but were reductively cleaved with Na/liquid NH_3.

EXPERIMENTAL

^{1}H NMR spectra were recorded with a Varian Gemini 200 or Bruker AM 500 spectrometer for solutions in benzene-d_6 or $CDCl_3$ (internal Me_4Si). Assignments of the signals were made on the basis of ^{1}H–^{1}H COSY and DEPT 135° experiments (for numbering of the protons see drawings in the text). Mass spectra (LSIMS; *m*-nitrobenzyl alcohol was used as a matrix to which sodium acetate was added) were recorded with an AMD-604 apparatus. Optical rotations were measured with a Digital Jasco polarimeter DIP-360 for solutions in $CHCl_3$ (*c* 1). Column chromatography was performed on silica gel (Merck, 70–230 or 230–400 mesh). CD spectra were measured between 650 and 230 nm at room temperature with a Jasco J715 spectropolarimeter using DMSO solutions in cells of 0.2 path length (spectral band width 1 nm, sensitivity 10×10^{-6} or 20×10^{-6} ΔA-unit/nm). Depending on the S/N-ratio the λ-scan speed was 0.2 or 0.5 nm/s. For CD measurements the chiral diol (1–3 mg) was dissolved in a solution of the stock $[Mo_2(OAc)_4]$ complex (6–7 mg) in DMSO (10 mL) so that the molar ratio of the stock complex to diol was about 1:0.3 to 1:0.7. As the true concentrations of the individual optically active complexes are not known, apparent $\Delta\varepsilon'$ values are given, calculated from the total ligand concentration and assuming 100% complexation. $[Mo_2(OAc)_4]$ and DMSO (Uvasol) were commercially available from Fluka AG and E. Merck, respectively, and were used without further purification. THF and methylene chloride were distilled from potassium and calcium hydride, respectively, prior to use. Dry toluene and diethyl ether were stored over sodium wire. For chromatography purposes a fraction of mineral oil with boiling point in a range 70–90°C was used as mixture of hexanes. All solutions were dried over anhydrous sodium sulfate. Acetylation reactions were performed under standard conditions: acetic anhydride, TEA, DMAP as a catalyst in dry methylene chloride.

General Procedure for Homologation of Sucrose at Either Terminal Position

Phosphonate **4**, **5**, **6** or **7** (1.5 mmol), aldehyde **1a**, **2a**, or **3a** (1.0 mmol, obtained by a Swern oxidation[11] of the corresponding alcohol **1, 2**, or **3**) or 1,2:3,4-di-*O*-isopropylidene- α-D-galactopyranos-6-ulose (for reaction with **7**) and 18-

crown-6 (6.0 mmol) were dissolved in dry toluene (50 mL) to which anhydrous potassium carbonate (3.0 mmol) was added. The mixture was stirred overnight at room temperature, water was added and the product was extracted with ethyl acetate. The organic phase was washed with water and brine, dried, concentrated and the product was isolated by column chromatography (hexanes − ethyl acetate, 6:1 to 2:1). Catalytic amounts of tetrabutylammonium bromide can also be used instead of 18-crown-6 without significant decrease in product yields.

2,3,4-Tri-*O*-benzyl-6-*O*-*p*-nitrobenzoyl-α-D-glucopyranosyl-(1↔9)-(*E*)-10,11-di-*O*-benzyl-7,8-dideoxy-13-*O*-*p*-nitrobenzoyl-1,2:3,4-di-*O*-isopropylidene-β-D-*xylo*-D-*galacto*-trideca-7-en-6,9-diulo-9,12-furanoside (8). (61%); [α] +7.7°; *m/z*: 1365 [M($C_{74}H_{74}N_2O_{22}$) + Na^+]. ^{1}H NMR (500 MHz, $CDCl_3$, selected signals) δ 7.07 and 7.00 (AB of H-7f and H-8f, 2H, J_{AB} = 15.5), 5.55 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1f), 5.35 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1g), 4.12 (broad d, 1H, H-5g), 4.00 (dd, 1H, H-3g), 3.51 (dd, 1H, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.9 Hz, H-4g), 3.42 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2g), 1.43, 1.28, 1.26, 1.17 [4×s, 4×3H, 2×C(CH_3)$_2$]. ^{13}C NMR (50 MHz, $CDCl_3$) δ 196.5 (C-6f), 164.2, 164.0 [2×*p*-O_2NPhC(O)O], 142.7 (C-8f), 126.5 (C-7f), 109.6, 108.9 [2×C(CH_3)$_2$], 104.7 (C-9f), 96.3, 91.8, 88.9, 82.6, 81.7, 79.5, 78.0, 76.8 (8×CH), 75.7, 75.0 (2×CH_2), 73.5 (CH), 72.9 (double intensity), 72.5 (3×CH_2), 72.3, 70.5, 70.2, 69.7 (4×CH), 66.1, 63.8 (2×CH_2), 25.9, 25.8, 24.7, 24.1 [2×C(CH_3)$_2$].

Anal. Calcd for $C_{74}H_{74}N_2O_{22}$: C, 66.16; H, 5.55; N, 2.09. Found: C, 66.4; H, 5.8; N, 2.1.

3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl-(2↔1)-(*E*)-2,3,4-tri-*O*-benzyl-6,7-dideoxy-10,11:12,13-di-*O*-isopropylidene-β-L-*galacto*-D-*gluco*-tridecadialdo-6-en-8-ulo-1,5-pyranoside (9). (82%); [α] −0.9°; *m/z*: 1425 [M($C_{84}H_{94}O_{17}Si$) + Na^+]. ^{1}H NMR, (500 MHz, $CDCl_3$, selected signals) δ 6.93 (dd, 1H, $J_{5,6}$ = 4.5 Hz, $J_{6,7}$ = 15.8 Hz, H-6g), 6.77 (dd, 1H, $J_{5,7}$ = 1.5 Hz, H-7g), 5.98 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1g), 5.45 (d, 1H, $J_{12,13}$ = 5.0 Hz, H-13g), 4.85–4.30 (m, 20H: 6×OCH_2Ph, OCH_2O, H-5g, H-3f, H-4f, H-11g, H-10g and H-9g), 4.25 (broad d, 1H, H-12g), 4.02 (dd, 1H, $J_{5,6a}$ = 3.5 Hz, $J_{6a,6b}$ = 11.3 Hz, H-6af), 3.49 (m, 1H, H-5f), 3.90 (dd, 1H, H-3g), 3.87 (dd, 1H, $J_{5,6b}$ = 4.4 Hz, H-6bf), 3.75 and 3.67 (AB of H-1af and H-1bf, 2H, J_{AB} = 11.1 Hz), 4.42 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2g), 3.17 (dd, 1H, $J_{3,4}$ = 9.1 Hz, $J_{4,5}$ = 10.0 Hz, H-4g), 1.40, 1.27, 1.23, 1.18 [4×s, 4×3 H, 2×C(CH_3)$_2$], 1.08 [s, 9H, SiC(CH_3)$_3$]. ^{13}C NMR (50 MHz, C_6D_6) δ 195.8 (C-8g), 144.6 (C-6g), 125.5 (C-7g), 109.5, 108.6 [2×C(CH_3)$_2$], 104.5 (C-2f), 96.9 (CH), 95.0 (OCH_2OCH_2Ph), 89.1, 84.2, 82.3, 82.2, 81.5, 81.4, 80.3 (7×CH), 75.6, 75.2 (2×CH_2), 73.8 (CH), 73.4, 73.1 (2×CH_2), 72.8 (CH), 72.5 (CH_2), 71.1 (double intensity), 71.0 (3×CH), 70.4, 69.5, 64.8 (3×CH_2), 27.3 (SiC(CH_3)$_3$), 26.2, 26.0, 24.7, 24.2 [2×C(CH_3)$_2$], 19.6 [SiC(CH_3)$_3$].

Anal. Calcd for $C_{84}H_{94}O_{17}Si·H_2O$: C, 70.96; H 6.81. Found: C, 70.3; H, 6.9.

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2,3,4-Tri-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-α-D-glucopyranosyl-(1↔12)-(*E*)-10,11-di-*O*-benzyl-7,8-dideoxy-13-*O*-benzyloxymethyl-1,2:3,4-di-*O*-isopropylidene-β-D-*lyxo*-D-*galacto*-trideca-7-en-6,12-diulo-9,12-furanoside (10). (86%); [α] −1.7°; *m/z*: 1425 [M($C_{84}H_{94}O_{17}Si$) + Na^+]. ^{1}H NMR, (500 MHz, $CDCl_3$, selected signals) δ 6.98 (dd, 1H, $J_{7,9}$ = 1.2 Hz, $J_{7,8}$ = 15.7 Hz, H-7f), 5.67 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1g), 5.51 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1f), 4.43 (ddd, 1H, $J_{8,9}$ = 5.9 Hz, H-9f), 4.37 (d, 1H, $J_{10,11}$ = 8.4 Hz, H-11f). 4.26 (d, 1H, $J_{2,3}$ = 1.2 Hz, H-2f), 4.17 (dd, 1H, $J_{9,10}$ = 8.5 Hz, H-10f), 3.77 and 3.68 (AB of H-13af and H-13bf, 2H, J_{AB} = 11.2 Hz), 3.65–3.56 (m, 2H, H-2g and H-4g), 1.46, 1.29, 1.27, 1.26 [4×s, 4×3H, 2×$C(CH_3)_2$], 1.00 [s, 9H, $SiC(CH_3)_3$]. ^{13}C NMR (50 MHz, C_6D_6) δ 195.9 (C-6f), 143.7 (C-8f), 126.2 (C-7f), 109.6, 108.8 [2×$\underline{C}(CH_3)_2$], 104.8 (C-12f), 96.8 (CH), 95.0 ($O\underline{C}H_2OCH_2Ph$), 90.2, 85.0, 83.9, 82.7, 81.1, 80.3, 78.1 (7×CH), 75.8, 75.2 (2×CH_2), 74.0 (CH), 73.5, 73.2 (2×CH_2), 73.1 (CH), 72.6 (CH_2), 72.5 71.1, 70.8 (3×CH), 70.0, 69.6, 63.2 (3×CH_2), 26.4 [$SiC(\underline{C}H_3)_3$], 25.3, 25.1, 23.8, 23.5 [2×$C(\underline{C}H_3)_2$], 18.8 [$Si\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{84}H_{94}O_{17}Si{\cdot}H_2O$: C, 70.96; H, 6.81. Found: C, 71.0; H, 6.9.

Benzyl (3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl)-(2↔1)-(*E*)-2,3,4,10,11,12-hexa-*O*-benzyl-6,7-dideoxy-α-L-*manno*-α-D-*gluco*-tridecadialdo-6-en-8-ulo-1,5:9,13-dipyranoside (11). (83%); [α] +73.2°; *m/z*: 1705 [M($C_{106}H_{110}O_{17}Si$) + Na^+]. ^{1}H NMR (500 MHz, $CDCl_3$, selected signals) δ 6.97 (dd, 1H, $J_{5,6}$ = 4.7 Hz, $J_{6,7}$ = 15.5 Hz, H-6g), 6.78 (dd, 1H, $J_{5,7}$ = 1.4 Hz, H-7g), 5.26 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1g), 3.77 and 3.69 (AB of H-1af and H-1bf, 2H, J_{AB} = 11.1 Hz), 3.44 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2g), 3.16 (dd, 1H, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.75 Hz, H-4g), 1.05 [s, 9H, $SiC(CH_3)_3$]. ^{13}C NMR (125 MHz, C_6D_6) δ 194.5 (C-8g), 145.1 (C-6g), 126.9 (C-7g), 104.7 (C-2f), 98.4 (CH), 94.9 ($O\underline{C}H_2OCH_2Ph$), 89.6, 84.3, 82.2, 82.01, 81.97, 81.7, 80.3, 79.9, 76.8, 76.2 (10×CH), 75.6 (CH_2), 75.4 (CH), 74.93, 74.88, 73.4, 73.1, 73.0, 72.6, 72.5 (7×CH_2), 71.0 (CH), 70.1, 69.7, 69.6, 65.2 (4×CH_2), 27.2 [$SiC(\underline{C}H_3)_3$], 19.5 [$Si\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{106}H_{110}O_{17}Si$: C, 75.60; H, 6.58. Found: C, 75.7; H, 6.5.

Methyl (3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl)-(2↔1)-(*E*)-2,3,4,12,13,14-hexa-*O*-benzyl-6,7-dideoxy-9,10-*O*-isopropy-lidene-β-L-*threo*-L-*altro*-α-D-*gluco*-pentadecadialdo-6-en-8-ulo-1,5:11,15-dipyranoside (12). (85%); [α] +33.8°; *m/z*: 1729 [M($C_{105}H_{114}O_{19}Si$) + Na^+]. ^{1}H NMR (500 MHz, $CDCl_3$, selected signals) δ 6.98 (dd, 1H, $J_{5,6}$ = 4.1 Hz, $J_{6,7}$ = 15.8 Hz, H-6g), 6.85 (dd, 1H, $J_{5,7}$ = 1.7 Hz, H-7g), 6.02 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1g), 3.77 and 3.69 (AB of H-1af and H-1bf, 2H, J_{AB} = 11.1 Hz), 3.42 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2g), 3.37 (s, 3H, OCH_3), 3.12 (dd, 1H, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 10.2 Hz, H-4g), 1.36, 1.12 [$C(CH_3)_2$], 1.07 [s, 9H, $SiC(CH_3)_3$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4 (C-8g), 145.6 (C-6g), 124.2 (C-7g), 110.4 [$\underline{C}(CH_3)_2$], 104.0 (C-2f), 97.7 (CH), 94.8 ($O\underline{C}H_2OCH_2Ph$), 88.7, 83.9,

82.7, 81.73, 81.69, 81.1, 80.6, 79.9, 79.8, 79.7, 78.2, 77.5 (12 × CH), 75.7, 75.6, 75.0, 74.6, 73.3, 73.2, 72.9, 72.1 (8×CH_2), 70.1 (CH), 69.91 (CH_2), 69.89 (CH), 69.5, 63.8 (2×CH_2), 55.0 (OCH_3), 27.0 [SiC($\underline{C}H_3)_3$], 26.4, 26.0 [C($\underline{C}H_3)_2$], 19.3 [Si$\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{105}H_{114}O_{19}Si{\cdot}H_2O$: C, 73.06; H, 6.77. Found: C, 73.0; H, 6.8.

3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl-(2↔1)-(*E*)-2,3,4-tri-*O*-benzyl-7,8-dideoxy-10,11:12,13-di-*O*-isopropylidene-β-L-*galacto*-D-*gluco*-tridecadialdo-7-en-6-ulo-1,5-pyranoside (13). (70%); [α] −14.7°; *m/z*: 1425 [M($C_{84}H_{94}O_{17}Si$) + Na^+]. ^{1}H NMR (500 MHz, $CDCl_3$, selected signals) δ 6.96 (dd, 1H, $J_{8,9}$ = 4.1 Hz, $J_{7,8}$ = 15.7 Hz, H-8g), 6.74 (dd, 1H, $J_{7,9}$ = 1.5 Hz, H-7g), 6.00 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1g), 5.45 (d, 1H, $J_{12,13}$ = 5.0 Hz, H-13g), 4.53 (dd, 1H, H-11g), 4.37 (ddd, 1H, H-9g), 4.25 (dd, 1H, $J_{11,12}$ = 2.4 Hz, H-12g), 4.15 (dd, 1H, $J_{10,11}$ = 7.8 Hz, $J_{9,10}$ = 2.1 Hz, H-10g), 3.74–3.64 (m, 3H, AB of H-1af and H-1bf, J_{AB} = 11.1 Hz and H-4g), 3.48 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2g), 1.39, 1.27, 1.23, 1.19 [4×s, 4×3H, 2×C($CH_3)_2$], 1.04 [s, 9H, SiC($CH_3)_3$]. ^{13}C NMR (50 MHz, C_6D_6) δ 194.7 (C-6g), 142.9 (C-8g), 109.5, 108.3 (2 × $\underline{C}(CH_3)_2$), 104.7 (C-2f), 96.7 (CH), 95.0 (O$\underline{C}H_2OCH_2Ph$), 89.7, 83.7, 82.3, 81.7, 81.6, 80.4, 79.5 (7×CH), 75.6, 75.0 (2×CH_2), 74.8 (CH), 73.1 (double intensity; 2×CH_2), 73.0 (CH), 72.6 (CH_2), 71.3 70.8, 68.2 (3×CH), 70.5, 69.5, 64.6 (3×CH_2), 27.3 [SiC($\underline{C}H_3)_3$], 26.3, 26.1, 24.7, 24.4 [2×C($\underline{C}H_3)_2$], 19.6 [Si$\underline{C}(CH_3)_3$].

Anal. Calcd for $C_{84}H_{94}O_{17}Si$: C, 71.87; H, 6.75. Found: C, 71.8; H, 6.6.

Functionalization of the Allylic Bridge in Higher Sucrose Enone 13

3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl-(2↔1)-(*E*)-2,3,4-tri-*O*-benzyl-7,8-dideoxy-10,11:12,13-di-*O*-isopropylidene-β-L-*glycero*-D-*gluco*-D-*gluco*-tridecadialdo-7-en-1,5-pyranoside (15). Enone 13 (1.5 g, 1.069 mmol) was dissolved in dry diethyl ether (50 mL) and cooled to 0°C. A solution of zinc borohydride[7,12] in diethyl ether was added until TLC (hexanes − ethyl acetate, 1:1) showed disappearance of the starting material and formation of a new, more polar product. The reaction mixture was diluted with ethyl acetate and excess of zinc borohydride was carefully decomposed with water. Organic phase was separated, washed with 2% sulfuric acid, then with aqueous sodium carbonate, water, brine and dried. Column chromatography (hexanes − ethyl acetate, from 6:1 to 3:1) gave 15 as the sole product. (1.24 g, 83%); [α] −2.3°; *m/z*: 1427 [M($C_{84}H_{96}O_{17}Si$) + Na^+]. ^{1}H NMR (200 MHz, C_6D_6, selected signals) δ 6.45–6.20 (m, 3H, H-1g, H-7g and H-8g), 5.55 (d, 1H, $J_{13,12}$ = 4.9 Hz, H-13g), 3.34 (broad d, 1H, $J_{6,OH}$ = 4.2 Hz, OH), 1.43, 1.38 [2×s, 2×3H, C($CH_3)_2$], 1.24 [s, 9H, SiC($CH_3)_3$], 1.08, 1.07 [2×s, 2×3H, C($CH_3)_2$]. ^{13}C NMR (50 MHz, C_6D_6) δ 109.2, 108.2 [(2×$\underline{C}(CH_3)_2$], 104.3 (C-2f), 96.9 (O$\underline{C}H_2OCH_2Ph$), 95.0, 88.7, 83.6, 81.1, 81.0, 80.9, 80.2, 79.3 (8×CH), 75.6, 75.0

(2×CH_2), 74.8, 74.4 (2×CH), 73.4, 73.3 (2×CH_2), 72.6 (CH), 72.4 (CH_2), 71.4 70.7, 69.4 (3×CH), 70.9, 69.6, 63.7 (3×CH_2), 27.3 [SiC($\underline{C}H_3)_3$], 26.5, 26.3, 25.0, 24.5 [2×C($\underline{C}H_3)_2$], 19.6 [(Si$\underline{C}$($CH_3)_3$].

3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructo-furanosyl-(2↔1)-2,3,4-tri-*O*-benzyl-D-*glycero*-α-D-glucopyranoside (16). Ozone was passed through a cooled (−78°C) and vigorously stirred solution of alcohol 15 (0.150 g, 0.107 mmol) in CH_2Cl_2/methanol (1:1 v/v, 30 mL) until a blue-green color persisted. Sodium borohydride (50 mg, 1.5 mmol) was added, and the mixture was allowed to attain room temperature. Water was added, and the product was extracted with ethyl acetate. The organic phase was washed with water, brine, dried, concentrated and the diol 16 was isolated by column chromatography (hexanes − ethyl acetate, from 3:1 to 1:1). (0.086 g, 68%); [α] +32.7°; *m/z*: 1203 [M($C_{72}H_{80}O_{13}Si$) + Na^+]. ^{1}H NMR (500 MHz, $CDCl_3$, selected signals) δ 6.05 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1g), 1.07 [s, 9H, SiC($CH_3)_3$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ 104.0 (C-2f), 94.9 (O$\underline{C}H_2OCH_2Ph$), 88.3 (C-1g), 83.2, 82.0, 80.3, 80.1 (double intensity), 79.0 (6×CH), 75.5, 74.7, 73.2, 72.9 (4×CH_2), 72.3 (CH), 72.0 (CH_2), 71.4 (CH), 70.3, 69.6, 63.1, 62.9 (4×CH_2), 26.9 [SiC($\underline{C}H_3)_3$], 19.2 (Si$\underline{C}$($CH_3)_3$). CD [λ(Δε′)]: 306.0 (+0.22), 351.0 (−0.07) nm.

Anal. Calcd for $C_{72}H_{80}O_{13}Si$: C, 73.20; H, 6.83. Found: C, 73.0; H, 7.0.

3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl-(2↔1)-(*E*)-2,3,4-tri-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-7,8-dideoxy-10,11:12, 13-di-*O*-isopropylidene-β-L-*glycero*-D-*gluco*-D-*gluco*-tridecadialdo-7-en-1,5-pyranoside (17). Alcohol **15** (0.925 g, 0.658 mmol), DMAP (40 mg, 0.033 mmol), imidazole (0.180 g, 2.644 mmol.), and *t*-butyldimethylsilyl chloride (0.120 g, 0.796 mmol) were dissolved in anhydrous DMF (15 mL) and stirred at 90°C for 2 h. Water was added and the product was extracted with ethyl acetate. The organic phase was washed with water, brine, dried, concentrated and ether **17** was isolated by column chromatography (hexanes − ethyl acetate from 8:1 to 3:1). (0.8825 g, 88%); [α] −3.1°; *m/z*: 1541 [M($C_{90}H_{110}O_{17}Si_2$) + Na^+]. ^{1}H NMR (500 MHz, C_6D_6, selected signals) δ 6.17 (dd, 1H, $J_{7,8}$ = 16.0 Hz, $J_{7,6}$ = 6.7 Hz, H-7), 6.08 (dd, 1H, $J_{8,9}$ = 7.1 Hz, H-8), 6.02 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.51 (d, 1H, $J_{13,12}$ = 5.0 Hz, H-13), 4.44 (dd, 1H, $J_{10,11}$ = 7.8 Hz, H-11), 4.39 (dd, 1H, H-9), 4.25 (dd, 1H, H-3), 4.14 (dd, 1H, $J_{11,12}$ = 2.3 Hz, H-12), 4.02 (broad s, 2H, H-1′a and H-1′b), 3.95 (broad t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 3.82 (dd, 1H, $J_{9,10}$ = 1.9 Hz, H-10), 3.59 (dd, 1H, $J_{2,3}$ = 9.7 Hz, H-2), 1.41, 1.36 [2×s, 2×3H, C($CH_3)_2$], 1.20 [s, 9H, SiC($CH_3)_3$], 1.08, 1.07 [2×s, 2×3H, C($CH_3)_2$], 1.05 [(s, 9H, SiC($CH_3)_3$], 0.18 [s, 6H, Si($CH_3)_3$($C\underline{H}_3)_2$]. ^{13}C NMR (50 MHz, C_6D_6) δ 109.0, 108.2 [2×$\underline{C}$($CH_3)_2$], 104.9 (C-2f), 96.7 (CH), 94.9 (O$\underline{C}H_2OCH_2Ph$), 90.3, 84.3, 83.4, 83.0, 82.3, 80.8, 78.4 (7×CH), 75.8 (CH_2), 75.7, 75.4 (2×CH), 74.9 (CH_2), 74.4 (CH), 73.1, 72.8, 72.7 (3×CH_2), 71.3 70.7, 69.1 (3×CH), 70.0, 69.5, 66.4 (3×CH_2), 27.26, 26.55 [2×SiC($\underline{C}H_3)_3$], 26.48, 26.25, 24.9, 24.4 [2×C($\underline{C}H_3)_2$], 19.6, 18.8 [2×Si$\underline{C}$($CH_3)_3$], −3.97, −4.03 [SiC($CH_3)_3$($\underline{C}H_3)_2$].

Anal. Calcd for $C_{90}H_{110}O_{17}Si_2 \cdot H_2O$: C, 70.28; H, 7.34. Found: C, 70.2; H, 7.4.

Dihydroxylation of 17. To a solution of 17 (0.8 g, 0.518 mmol) in THF (8.0 mL), *t*-butyl alcohol (0.8 mL) and water (0.1 mL) *N*-methylmorpholine *N*-oxide (0.160 g, 1.2 mmol) and OsO_4 (0.5 mL of a ca 2% solution in *t*-butyl alcohol) were added, and the mixture was stirred for 24 hours at room temperature. Methanol (20 mL) and saturated aqueous sodium hydrogen sulfite (3 mL) were added and stirring was prolonged for another 1 hour. The reaction mixture was filtered through Celite and the products were extracted with ethyl acetate. The organic phase was washed with water, brine, dried, concentrated and the products were separated using preparative HPLC. Retention times for 18 and 19 are 1.98 and 2.42 min, respectively (Shimadzu LC-8A liquid chromatograph, Shimadzu SPD-6A UV detector, and column from Machery-Nagel: Nucleosil 100-7; phase: hexanes − ethyl acetate, 3:1 with constant flow rate: 4 mL/min).

3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl-(2↔13)-10,11,12-tri-*O*-benzyl-8-*O*-*t*-butyldimethylsilyl-1,2:3,4-di-*O*-isopropylidene-β-L-*xylo*-L-*altro*-D-*galacto*-tridecadialdo-9,13-pyranoside (18). (40%); [α] −5.1°; *m/z*: 1575 [$M(C_{90}H_{112}O_{19}Si_2) + Na^+$]. ^{1}H NMR (500 MHz, C_6D_6, selected signals) δ 5.97 (d, 1H, $J_{12,13}$ = 3.5 Hz, H-13g), 5.46 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1g), 4.20 (dd, 1H, $J_{2,3}$ = 2.3 Hz, H-2g), 3.65 (dd, 1H, $J_{11,12}$ = 9.7 Hz, H-12g), 3.15 (broad s, 1H, OH), 2.92 (broad d, 1H, OH), 1.49, 1.33 [2×s, 2×3H, $C(CH_3)_2$], 1.27, 1.16 [2×s, 2×9H, 2×$SiC(CH_3)_3$], 1.11, 1.06, [2×s, 2×H, $C(CH_3)_2$], 0.36, 0.35 [2×s, 2×3H, 2×$Si(CH_3)_2(C\underline{H}_3)_2$]. ^{13}C NMR (125 MHz, C_6D_6) δ 109.1, 108.5 [2×$\underline{C}(CH_3)_2$], 104.3 (C-2f), 96.6 (CH), 94.4 ($O\underline{C}H_2OCH_2Ph$), 90.3, 84.1, 83.7, 82.8, 82.6, 80.6, 78.1, 76.2 (8×CH), 75.5, 74.9, 72.82, 72.79, 72.56 (5×CH_2), 71.3, 71.1, 71.0, 70.9, 70.8, 69.7, 69.5 (7×CH), 69.1, 68.9, 67.3 (3×CH_2), 27.0, 26.3 [2×$SiC(\underline{C}H_3)_3$], 26.0, 25.8, 24.7, 24.0 [2×$C(\underline{C}H_3)_2$], 19.3, 18.5 [2×$Si\underline{C}(CH_3)_3$], −3.7, −4.7 [$(SiC(CH_3)_3(\underline{C}H_3)_2$]. CD [λ(Δε′)]: 304.5 (+0.14), 352.5 (−0.02) nm.

Anal. Calcd for $C_{90}H_{112}O_{19}Si_2$: C, 69.56; H, 7.26. Found: C, 69.5; H, 7.2.

3,4-Di-*O*-benzyl-1-*O*-benzyloxymethyl-6-*O*-*t*-butyldiphenylsilyl-β-D-fructofuranosyl-(2↔13)-10,11,12-tri-*O*-benzyl-8-*O*-*t*-butyldimethylsilyl-1,2:3,4-di-*O*-isopropylidene-β-L-*xylo*-L-*gluco*-D-*galacto*-tridecadialdo-9,13-pyranoside (19). (40%); [α] −2.7°; *m/z*: 1575 [$M(C_{90}H_{112}O_{19}Si_2) + Na^+$]. ^{1}H NMR (500 MHz, C_6D_6, selected signals) δ 5.89 (d, 1H, $J_{12,13}$ = 3.6 Hz, H-13g), 5.42 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1g), 4.18 (dd, 1H, $J_{2,3}$ = 2.4 Hz, H-2g), 3.64 (dd, 1H, $J_{11,12}$ = 9.7 Hz, H-12g), 3.02 (broad d, 1H, OH), 1.89 (broad d, 1H, OH), 1.50, 1.40, 1.19 (3×s, 3×3H, $C(CH_3)_2$], 1.17 [s, 9H, $SiC(CH_3)_3$], 1.09 [s, 12H, $SiC(CH_3)_3$ and one of $C(CH_3)_2$], 0.28, 0.24 [2×s, 2×3H, $Si(CH_3)_3(C\underline{H}_3)_2$]. ^{13}C NMR (125 MHz, C_6D_6) δ 108.7, 108.3 [2×$\underline{C}(CH_3)_2$], 104.7 (C-2f), 96.6 (CH), 94.6 ($O\underline{C}H_2OCH_2Ph$), 89.9, 84.1, 83.7, 83.0, 82.3, 80.5, 76.9 (7×CH), 75.5, 75.4 (2×CH_2), 73.9 (CH), 72.80, 72.75, 72.46 (3×CH_2), 71.3, 71.2, 71.1, 70.9, 70.6

(5×CH), 69.31, 69.28 (2×CH_2), 68.8, 67.1 (2×CH), 66.5 (CH_2), 26.9, 26.4 [2×SiC($\underline{C}H_3)_3$], 26.2, 26.0, 25.0, 24.2 [2×C($\underline{C}H_3)_2$], 19.3, 18.5 [2×Si$\underline{C}(CH_3)_3$], −3.1, −5.2 [SiC$(CH_3)_3(\underline{C}H_3)_2$]. CD [λ(Δε′)]: 321.5 (−0.06), 428.5 (+0.01) nm.

Anal. Calcd for $C_{90}H_{112}O_{19}Si_2$: C, 69.56; H, 7.26. Found: C, 69.8; H, 7.2.

1,3,4,6-Tetra-*O*-acetyl-β-D-fructofuranosyl-(2↔13)-6,7,10,11,12-penta-*O*-acetyl-8-*O*-*t*-butyldimethylsilyl-1,2:3,4-di-*O*-isopropylidene-β-L-*xylo*-L-*gluco*-D-*galacto*-tridecadialdo-9,13-pyranoside (20). Diol **19** (0.180 g, 0.116 mmol) was dissolved in anhydrous THF (10 mL) and liquid ammonia (30 mL) at −78°C. During stirring sodium was added in small pieces until deep blue color persisted for 30 min. Excess sodium was decomposed by addition of solid ammonium chloride and the reaction mixture was allowed to attain room temperature (ca 16 h). After evaporation of ammonia, the reaction mixture was concentrated in vacuum and the residue was acetylated. Column chromatography (hexanes − ethyl acetate, from 4:1 to 1:2) afforded the desired product **20** (0.075 g, 58%); [α] +17.9°; *m/z*: MS: 1145 [M($C_{49}H_{74}O_{27}Si$) + Na^+]. ^{1}H NMR (500 MHz, $CDCl_3$, selected signals) δ 5.59 (d, 1H, $J_{12,13}$ = 3.6 Hz, H-13g), 5.43 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1g), 5.30 (m, 1H, H-5f), 4.80 (dd, 1H, $J_{11,12}$ = 10.0 Hz, H-12g), 4.52 (dd, 1H, $J_{3,4}$ = 8.2 Hz, H-3g), 4.43 (m, 1H, H-6af), 4.23 (dd, 1H, $J_{2,3}$ = 2.0 Hz, H-2d), 4.05 (a part of AB, 1H, J_{AB} = 11.9 Hz, H-1bf), 2.18, 2.14, 2.12, 2.10, 2.09, 2.08, 2.07, 2.05, 1.87 [9×s, 9×3H, 9×C(O)CH_3], 1.56, 1.39, 1.28, 1.26 [4×s, 4×3H, 2×C$(CH_3)_2$], 0.93 [s, 9H, SiC$(CH_3)_3$], 0.19, 0.18 [2×s, 2×3H, 2×Si$(CH_3)_3(C\underline{H}_3)_2$]. ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 170.3, 170.2, 170.01, 169.99, 169.8, 169.7, 169.4, 169.1 [9×O$\underline{C}$(O)CH_3], 108.7, 108.2 [2×$\underline{C}(CH_3)_2$], 103.9 (C-2f), 95.8, 90.2, 79.0, 75.9, 75.7, 72.5, 71.4, 70.6, 70.50, 70.47, 70.3, 70.2, 69.9, 69.7, 67.7, 67.0 (16×CH), 64.5, 63.6 (2×CH_2), 26.2 [SiC($\underline{C}H_3)_3$], 25.8, 25.7, 24.9, 23.6 [2×C($\underline{C}H_3)_2$], 20.73, 20.71 (triple intensity), 20.67 (double), 20.63 (double), 20.45 [9×OC(O)$\underline{C}H_3$], 18.2 [Si$\underline{C}(CH_3)_3$], −3.1, −4.9 [SiC$(CH_3)_3$-$(\underline{C}H_3)_2$].

Anal. Calcd for $C_{49}H_{74}O_{27}Si$: C, 52.40; H, 6.64. Found: C, 52.5; H, 6.6.

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