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Synthesis of Phosphorylated Derivatives of Sucrose: 6,6'-di-Phosphonate, 6- and 6'-Phosphonates, and 6,6'-di-Phosphine

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Reaction of 6,6'-dideoxy-6,6'-di-iodo-1',2,3,3',4,4'-hexa-*O*-benzylsucrose with triethyl phosphite afforded the corresponding 6,6'-diphosphonate. Selective phosphonylation either at the C-6 or 6-6' position was also possible providing the corresponding sucrose mono-phosphonates. Reaction of 6,6'-dichloro-hexa-*O*-benzylsucrose with diphenylphosphine anion afforded the 6,6'-diphosphinosucrose.

Keywords Sucrose; Sucrose phosphonates; Sucrose phosphines

Sucrose (α -D-fructofuranosyl β -D-glucopyranoside), the most available low-weight carbohydrate, is absorbed mostly by the food market, but efforts have also been put forward to use this compound as a chemically reactive organic raw material.^[1–3] The main problems encountered during work with sucrose are very high sensitivity of the glycosidic bond toward acids,^[1,4] poor solubility in organic solvents, and similar reactivity of the eight hydroxyl groups present in the molecule. Only differentiation between the primary and secondary OH groups is relatively straightforward: 1',6,6'-tri-*O*-trityl^[5] and 1',6,6'-tri-*O*-silylated^[6,7] sucroses are obtained in good yields by reaction of sucrose with an excess of trityl or silyl chlorides. It is also worth pointing out the very high affinity of the 6'-OH group toward the silylating agents, which allows preparing 6'-*O*-monoprotected sucrose in good yield.^[7]

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As a part of an ongoing program in the application of sucrose as a fine chemical, we have elaborated a convenient route to 1',2,3,4,3',4'-hexa-*O*-benzylsucrose (**1**),^[2] in which all secondary hydroxyl groups and the less reactive primary one (at the C1'-position) were protected with the benzyl blocks easily removable under neutral conditions. The diol **1** is a convenient starting material for the preparation of crown and aza-crown ether analogues,^[2,8] showing interesting complexing abilities toward the ammonium cation^[8] and significant enantioselectivity in complexation of α -phenylethylamine (e.g., **2**; X = Y = Z = NBn).^[9]

Diol **1** was also used for the preparation of sulphated sucroses. Either the bi-sulphide (**3**)^[10] or the monosulphide (**4**) was obtained; the latter was easily dimerized to the disulphide (**6**),^[11] which can be used for the preparation of the sulphated macrocycles with sucrose scaffold (Fig. 1).

The diol **1**, which is used for the synthesis of compounds of type **2–6**, is prepared from di-*O*-tritylsucrose **7**, obtained by selective tritylation of free sucrose. However, isolation of the intermediate **7** requires extensive chromatographic purification.^[2] We have succeeded now in an efficient isolation of di-*O*-tritylsucrose **7** without any chromatographic method. Also, the hydrolysis of the trityl ethers in **8** was optimized (Sch. 1; for detailed procedure see Experimental).

Exploring the chemistry of sucrose, we turned our attention to the phosphorous analogues of this disaccharide. Sucrose phosphines might be, eventually, applied as ligands in asymmetric synthesis.^[12] On the other hand, the sucrose phosphonates are important targets, since some of them [with the C(6)–O–P–C bond] possess very interesting biological activity.^[13]

The Arbuzov reaction was designed to prepare the phosphonate analogues of sucrose. Hexa-*O*-benzyl-6,6'-di-chlorosucrose (**9**)^[10] seemed to be the most

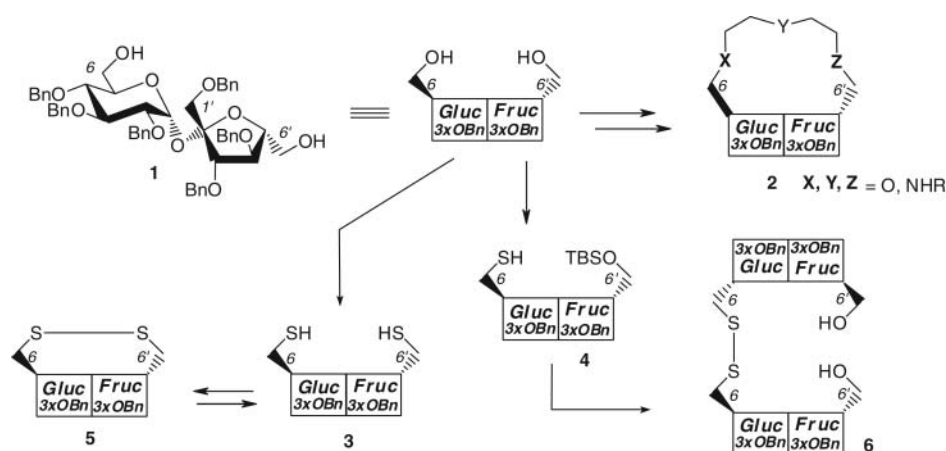
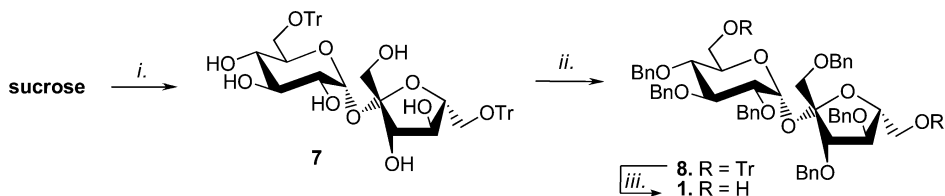
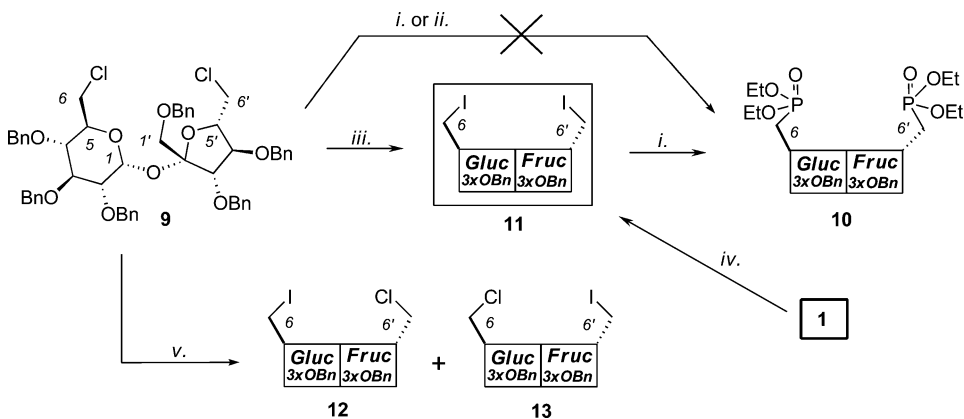


Figure 1: Synthesis of fine chemicals from sucrose.



Scheme 1: i. TrCl, DMAP (cat.), py, r.t., 44%; ii. BnBr, NaH, DMF, r.t., 93%; iii. I₂/MeOH, CH₂Cl₂, reflux, 42%.

convenient starting material for the model preparation of the di-phosphonate **10**, but reaction of this compound either with triethyl or diethyl trimethylsilyl phosphite did not afford any product. We decided, therefore, to apply the di-iodosucrose **11**, easily prepared from the corresponding diol **1**, under the standard conditions (see Experimental section); this compound was also prepared from dichloro-derivative **9** by reaction with excess potassium iodide. Reaction of the di-iodo derivative **11** with excess (EtO)₃P afforded the desired di-phosphonate **10** in 24% yield (Sch. 2).



Scheme 2: i. (EtO)₃P, reflux, 24 h; ii. (EtO)₂P(OTMS), 60°C, 48 h; iii. KI (excess), DMF, 120°C, 72 h, 66%; iv. 1. MsCl, Et₃N, DMAP, CH₂Cl₂, r.t. 85%; 2. KI (excess, DMF, 90°C, 36 h, 98%; v. KI (1 equiv.), DMF, 120°C, 12 h ratio 12 : 13 = 25 : 1 (23% 12).

It is known that the 6- and 6'-positions in sucrose have different reactivity toward some reagents (such as silyl chlorides). We have observed similar regioselectivity in reaction of di-chloride with iodide anion, which might open a convenient route to sucrose mono-phosphorous derivatives.

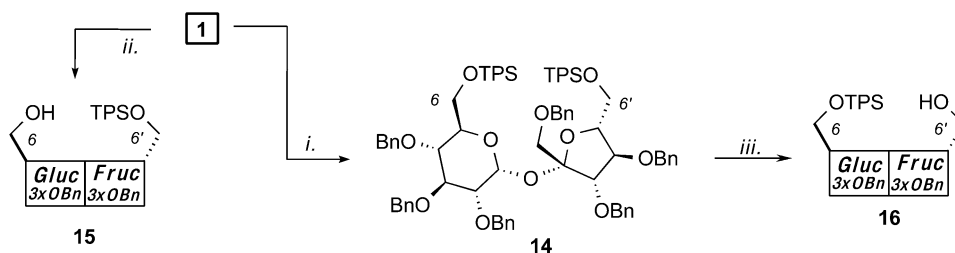
Reaction of **9** with one equiv. of KI afforded a mixture of mono-iodides **12** and **13** with the preponderance of the 6-iodo-6'-chloro-derivative **12**. These two regioisomers could not, however, be separated even by HPLC, so the assignment of their structure was performed on the mixture.

In the mass spectrum, the signal *m/z* 1033 was found, which could be assigned to chloro-iodo-hexa-*O*-benzyl-sucrose [M (C₅₄H₅₆ClIO₉)+Na⁺ = 1010 + 23]. Two signals of the H-1 protons from **12** and **13** (at δ = 5.68 and 5.64 ppm)

allowed us to establish the ratio of both regioisomers at 2.5:1. The position of iodine at the “glucose end” (C6) was determined by NMR correlations. The anomeric proton in the main isomer ($\delta = 5.68$ ppm) could be (via COSY cross-peaks) connected to the H5 (m, $\delta = 3.40$), which correlated to both H6 of the glucose part at δ : 3.29 (dd, 1H, $J_{6a,4} = 3.9$, $J_{6b,6a} = 10.9$ Hz) and 3.20 (dd, 1H, $J_{6b,4} = 2.8$ Hz) ppm. The HETCOR spectrum showed the cross-peaks of these two protons to the carbon resonance at $\delta = 9.31$ ppm, which was assigned to the $-\text{CH}_2-\text{I}$ group. Analogously, the H-1 signal of the minor regioisomer **13** (at $\delta = 5.64$ ppm) could be correlated with the ^{13}C resonance at $\delta = 6.15$ ppm, which had much lower intensity than the signal at $\delta = 9.32$ ppm. Thus, the major isomer had structure **12** and, consequently, structure **13** was assigned to the minor one.

Because we were not able to isolate these two regioisomers in pure form, another route to sucrose monophosphonates was elaborated.

The synthesis was initiated from the diol **1**. Taking advantage of the known affinity of the 6'-OH toward the silylating agents (either in free^[7] or partially protected sucrose^[2,14]), the monoalcohol **15** was prepared in good yield.^[14] The regioisomeric (to **15**) alcohol **16** was prepared by selective desilylation* of the double protected derivative **14** as shown in Scheme 3.

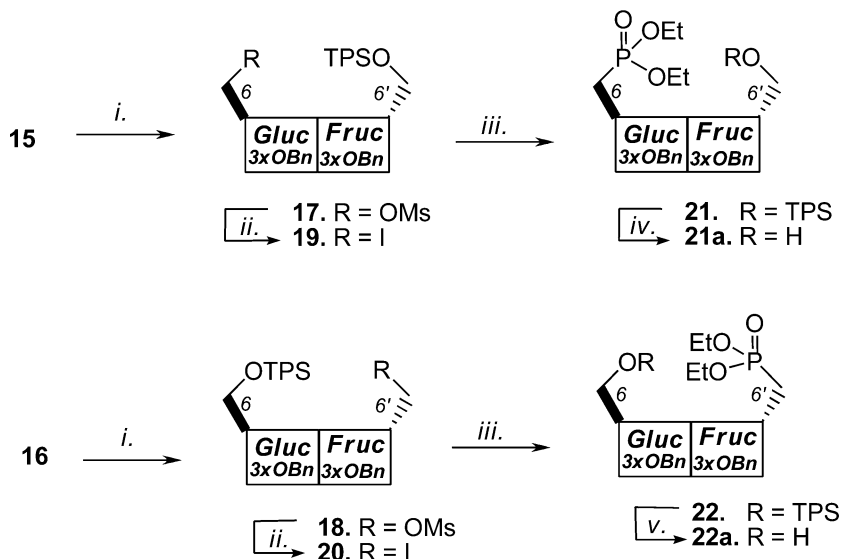


Scheme 3: i. TPSCI (2.5 equiv.), DIPEA, DMAP (cat), CH₂Cl₂, r.t., 80%; ii. TPSCI (2 equiv.), DIPEA, DMAP (cat.), CH₂Cl₂, r.t., 62%; iii. Bu₄NF·3H₂O, THF, r.t. 58%.

Synthesis of both monophosphates was performed according to the same methodology. Thus, activation of the hydroxyl group either in **15** or **16** provided the corresponding mesylates **17** and **18**, which were then converted into iodides **19** and **20** by reaction with potassium iodide. Further reaction of these intermediates with triethyl phosphite performed under reflux afforded finally the desired (mono-silylated) phosphonates **21** (87% yield) and **22** (45% yield).

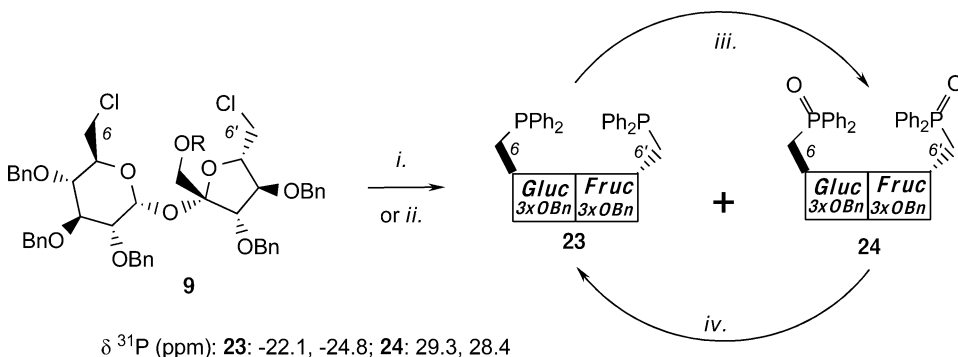
Removal of the silyl protection from the 6-phosphonate **21** was possible and afforded the free alcohol **21a** in good yield. Much more difficult was deprotection of the regioisomeric phosphonate **22**; under the standard conditions only traces of alcohol **22a** (detectable by MS) were obtained (Sch. 4).

Next we turned our attention to the synthesis of sucrose phosphines, which were initiated from the perbenzylated dichlorosucrose **9**, readily available in



Scheme 4: i. MsCl, py, r.t. (87% of 17, 93% of 18); ii. KI, DMF, 120°C, (89% of 19, 44% of 20); iii. (EtO)₃P, reflux, (88% of 21, 45% of 22); iv. Bu₄NF · 3H₂O, THF, 60°C, 74%; v. Bu₄NF, KOH, MeOH, r.t., traces.

our laboratory.^[10] Reaction of **9** with the diphenylphosphine anion (generated from either Ph₂PH/Na^[15] or Ph₃P/Na^[16]) afforded sucrose diphosphine **23**, which usually was contaminated with the oxidation product **24**. Presence of both species was detected easily by the ³¹P NMR spectra in which the characteristic signals for phosphine $\delta = -22.1$ and -24.8 ppm in **23** and phosphine oxide $\delta = +29.3$ and $+28.4$ ppm in **24** were seen (Sch. 5).



Scheme 5: i. Ph₃P/Na, THF, 30 min. r.t., then **9**, overnight (29% of **23**); ii. Ph₂PH/Na, THF, 30 min. then **9** overnight r.t. (5% of **23**, 27% of **24**); iii. Mel, then LAH, THF, r.t., 24 h, 49%; iv. H₂O₂, acetone, r.t., 24 h, quant.

The undesired di-phosphine oxide **24** was easily reduced to di-phosphine **23** with lithium aluminum hydride. Alternatively, the phosphine **23** was quantitatively oxidized to di-oxide **24** with hydrogen peroxide (see Experimental section).

CONCLUSION

Proper functionalization of the C-6 and C-6' "ends" in hexa-*O*-benzyl sucrose provided the phosphorous analogues of sucrose, either phosphonates or phosphines. Regioselective introduction of the phosphorous atom either at the C-6 or C-6' positions was also performed in good yield. The methodology presented in this paper allows for the introduction of the phosphorous atom at both (C-6 and C-6') terminal positions and also preparation of sucrose mono-phosphates.

EXPERIMENTAL

The NMR spectra were measured in CDCl₃ solutions (internal Me₄Si) with the following spectrometers: Bruker DRX 500, Varian-NMR-vnmrs600, and Varian Merkurs 400. The assignment of the ¹H and ¹³C NMR signals was made using results of 2D methods including COSY, HSQC, and DEPT correlations. The ¹H and ¹³C aromatic resonances occurring at the typical δ values were omitted for simplicity. In the ¹H NMR spectra only diagnostic signals are shown. Mass spectra were recorded with an ESI/MS Mariner (PerSeptive Biosystem) mass spectrometer. Optical rotations were measured with a Jasco P-1020 or P-2000 polarimeter ($\lambda = 589$ nm) for solutions in CHCl₃ ($c = 1$) at rt (unless otherwise stated). Column chromatography was performed on silica gel (Merck, 70–230 mesh). Methylene chloride was distilled from CaH₂ and THF from potassium prior to use. Organic solutions were dried over anhydrous magnesium or sodium sulphate.

Improved preparation of 1,2,2',3,3',4,4'-hexa-*O*-benzylsucrose (**1**)

*Synthesis of 6,6'-di-*O*-tritylsucrose (7)*

A suspension of sucrose (10 g, 29 mmol) in pyridine (170 mL) was boiled under reflux until all material dissolved (10 min) and the clear solution was cooled to rt. Trityl chloride (19 g, 68 mmol) and a catalytic amount of DMAP (0.1 g) were added and the reaction mixture was stirred at rt for 3 days. After this time TLC (ethanol/ethyl acetate/water, 45:5:3) indicated formation of the desired (previously synthesized ref. [10,17]) di-*O*-tritylsucrose **3** and side products (tri-*O*-trityl and several mono-*O*-trityl derivatives). An excess of pyridine was removed under reduced pressure, and the residue was partitioned between

water (200 mL) and ethyl acetate (200 mL). The organic solution was separated and the aqueous phase extracted with ethyl acetate (2×200 mL). Combined organic solutions were dried and concentrated, and a syrupy residue was partitioned between toluene (200 mL) and methanol/water (200 mL, 1:1 *v/v*). Two phases were separated; toluene one was collected and aqueous/methanolic was discarded. Toluene phase (containing **7**, tri-*O*-trityl-sucroses, trityl chloride, and trityl alcohol) was washed with aqueous methanol (3×200 mL, 1:1 *v/v*), dried, and concentrated. The residue—a yellowish foam—was dissolved in toluene (90 mL), to which methanol (130 mL) and water (40 mL) were added. Two phases were formed. The aqueous methanolic phase (containing mostly the desired **7**) was separated and the toluene one extracted with aqueous methanol (2×170 mL, 3:1 *v/v*). Combined methanolic fractions were concentrated, the residue was dissolved in a small amount of methanol, and **7** crystallized. The white product crystals formed were filtered and dried to afford the title derivative **7** in 44% yield. $[\alpha]_{\text{D}} = 39.5$.

The six hydroxyl groups in **7** were protected as benzyl ethers (to provide **8**) as described previously.^[18]

Removal of trityl blocks from 8

Usually this deprotection is performed with acetic acid.^[10,18] However, the procedure sometimes may cause problems resulting from hydrolysis of the glycosidic bond. The new procedure described below allowed us to obtain the desired diol **1** with full reproducibility. Thus, a solution of 6,6'-ditryl-1',2,3,3',4,4'-hexa-benzylsucrose (**8**, 4.11 g, 3 mmol) was dissolved in methylene chloride (5 mL), to which a 5% solution of iodine in methanol (50 mL) was added and the mixture was stirred and boiled under reflux for 3.5 h. After cooling to rt, aq. $\text{Na}_2\text{S}_2\text{O}_3$ was added, followed by ethyl acetate (300 mL). The organic phase was separated, washed with aq. 10% NaOH (until neutrality), dried, and concentrated, and the product was isolated by column chromatography (ethyl acetate/hexane, 1.5:1) to afford the desired diol **1** as colorless oil (1.09 g, 1.2 mmol, 42%), identical in all respects with the product prepared by the independent route.^[13,17]

$$[\alpha]_{\text{D}} = 41.2 (\text{lit. } [\alpha]_{\text{D}} = 40.8).^{[17]}$$

1,2,2',3,3',4,4'-Hexa-*O*-benzyl-6,6'-dideoxy-6,6'-di-iodosucrose (11)

Method a: To a stirred solution of 6,6'-dideoxy-6,6'-di-chloro-1,2,2',3,3',4,4'-hexa-*O*-benzylsucrose^[10] (**9**) (2.11 g, 2.3 mmol) in dry DMF (20 mL), potassium iodide (3 g) was added, and the mixture was stirred at 120°C for 72 h and cooled to rt. Water (30 mL) was added and the product was extracted with diethyl ether (3×50 mL). Combined organic solutions were

dried and concentrated, and the product **11** was isolated by column chromatography (hexane/ethyl acetate, 8:1) as a colorless oil (1.66 g, 1.5 mmol, 66%).

$[\alpha]_D = 25.3$; m/z : 1125.1913 [calcd. for $C_{54}H_{56}O_9NaI$ (M+Na): 1125.1906]; 1H NMR (500 MHz) δ : 5.64 (d, 1H, $J = 3.6$ Hz, H-1); ^{13}C NMR δ : 138.6, 138.4, 138.1, 138.0, 137.8 double intensity ($6 \times C_{quat.}$ O-CH₂-Ph), 105.3 (C-2'), 90.3, 85.2, 84.6, 81.6, 81.2, 80.6, 80.0, 69.0 (C-1, C-3', C-4', C-5', C-2, C-3, C-4, C-5), 75.5, 75.2, 73.5, 73.1, 72.5 double intensity, 70.8 ($6 \times$ O-CH₂-Ph, C-1'), 9.5 and 6.3 (C-6', C-6).

Anal. calc. for $C_{54}H_{56}O_9I_2$: C, 58.81; H, 5.12; found: C, 58.67; H, 5.27%.

Method b: To a stirred solution of the diol **1** (0.2 g, 0.23 mmol) in dichloromethane (8 mL), triethylamine (0.1 mL, 1.4 mmol) and a catalytic amount of DMAP (20 mg) were added. Mesyl chloride (0.1 mL, 1.2 mmol) was added dropwise, the mixture was kept 24 h at rt and then partitioned between water (20 mL) and ethyl acetate (30 mL). The organic phase was separated and the aqueous one extracted with ethyl acetate (2×30 mL). Combined organic solutions were dried and concentrated, and the product was purified by column chromatography (hexane/ethyl acetate, 5:1 then 2:1) to afford the corresponding di-mesylate^[13] as a colorless oil (0.2 g, 0.2 mmol, 85%).

To a solution of this mesylate (0.11 g, 0.1 mmol) in dry DMF (5 mL), KI (0.17 g, 1 mmol) was added, and the mixture was stirred at 90°C for 36 h and after cooling to rt partitioned between water (15 mL) and diethyl ether (15 mL). The organic phase was separated and the aqueous one extracted with diethyl ether (2×15 mL). Combined organic solutions were dried and concentrated, and the product **11** was purified by column chromatography (hexane/ethyl acetate, 8:1) as a colorless oil (0.11 g, 0.1 mmol, 96%).

6,6'-bis-(Diethoxy-phosphoryl)-6,6'-dideoxy-1',2,3,3',4,4'-hexa-O-benzylsucrose (10)

Compound **11** (1.5 g, 1.4 mmol) was dissolved in $P(OEt)_3$ (7 mL), stirred, and boiled under reflux in the oxygen-free atmosphere for 72 h. The excess of $P(OEt)_3$ was removed under vacuum (below 70°C) and the product was purified by column chromatography (hexane/ethyl acetate, 2:1) to afford **10** as a colorless oil (0.37 g, 0.33 mmol, 24%).

$[\alpha]_D = 21.7$; m/z 1145.4537 [calc. for $C_{62}H_{76}O_{15}P_2Na$ (M+Na): 1145.455; 1H NMR (500 MHz) δ : 5.65 (d, 1H, $J = 3.5$ Hz; H-1); ^{31}P NMR δ : 29.81, 29.10; ^{13}C NMR δ : 138.7, 138.6, 138.3, 138.23, 138.21, 138.1 ($6 \times C_{quat.}$ O-CH₂-Ph), 105.3 (C-2'), 90.3, 85.9 (d, $J_{CP} = 12.2$ Hz), 84.0 (d, $J_{CP} = 1.9$ Hz), 81.6, 81.0 (d, $J_{CP} = 9.4$ Hz), 80.0, 76.1 (d, $J_{CP} = 3.4$ Hz), 67.0 (d, $J_{CP} = 7.0$ Hz) (C-1, C-3', C-4', C-5', C-2, C-3, C-4, C-5), 75.3, 74.7, 73.3, 73.0, 72.7, 72.3, 70.9 ($6 \times$ O-CH₂-Ph, C-1'), 61.7 (d, $J_{CP} = 6.2$ Hz), 61.5 (d, $J_{CP} = 6.2$ Hz), 61.4 (d, $J_{CP} = 6.2$ Hz), 61.2 (d, $J_{CP} = 6.0$ Hz), 31.9 (d, $J_{CP} = 139$ Hz), 27.8 (d, $J_{CP} = 142$ Hz) ($4 \times$ P-OCH₂-CH₃, C-6, C-6'), 32.2, 16.4 (m, $4 \times$ P-OCH₂-CH₃).

Anal. xalc. for $C_{62}H_{76}O_{15}P_2 \cdot 0,5 H_2O$: C, 65.77; H, 6.85; found: C, 65.77; H, 6.57%.

6,6'-Dideoxy-6'-chloro-6-iodo- and 6,6'-dideoxy-6-chloro-6'-iodosucrose and 1,2,2',3,3',4,4'-hexa-O-benzyl- sucrose (12 and 13)

Di-chloro derivative **9** (0.6 g, 0.65 mmol) was dissolved in DMF (7.5 mL), to which KI (0.11 g, 0.65 mmol) was added and the mixture stirred at 120°C for 12 h. After cooling to rt, water (15 mL) was added and product was extracted with diethyl ether (3 × 15 mL). Combined organic solutions were dried and concentrated, and the product was isolated by HPLC (C18-column, hexane/ethyl acetate, 10:1) to afford an unseparable mixture of regioisomers **12** and **13** as a colorless oil (210 mg, 0.21 mmol, 32%) in the 2.5:1 ratio.

$$m/z : 1033 [M(C_{54}H_{56}O_9ClI + Na^+ = 1010 + 23)].$$

NMR data for mixture of isomers **12** and **13**: 1H NMR (500 MHz) δ : 5.68 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1; main isomer **12**), 5.65 (d, 1H, $J_{1,2} = 3.5$ Hz, H-1; minor isomer **13**); ^{13}C NMR δ : 105.3 and 105.2 (C-2' of **12** and C-2' of **13**), 90.3 (C-1 of **12** and C-1 of **13**), 45.0 (C-6' of **12** and C-6 of **13**), 9.32 (much higher intensity C-6 of **12**), and 6.15 (lower intensity C-6' of **13**).

Other selected 1H NMR signals of the main isomer **12**: 4.0 (m, H-3), 3.52 (m, H-2), 3.40 (m, H-4, H-5), 3.29 and 3.20 (both H-6).

1,2,2',3,3',4,4'-Hexa-O-benzyl-6,6'-di-O-(*tert*-butyldiphenylsilyl) sucrose (14).

Compound **1** (5 g, 5.7 mmol) was dissolved in dry methylene chloride (18 mL) containing DMAP (cat.) and DIPEA (2 mL, 11.7 mmol). *tert*-Butyldiphenylsilyl chloride (3 mL, 11.6 mmol) was added dropwise and the mixture was stirred for 12 h at rt. Then it was partitioned between water (15 mL) and ethyl acetate (20 mL), the organic phase was separated, and the aqueous one was extracted with ethyl acetate (2 × 20 mL). Combined organic solutions were dried and concentrated, and the product was purified by column chromatography (hexane/ethyl acetate, 5:1 to 3:1) to afford **11** as a colorless oil (6.2 g, 4.6 mmol, 80%). Significant amounts (1.14 g, 1.0 mmol, 18%) of 1,2,2',3,3',4,4'-hexa-O-benzyl-6'-O-(*tert*-butyldiphenylsilyl)sucrose^[14] (**15**) were also formed.

Data for **14**: $[\alpha]_D = 26.0$; m/z : 1383 $[M(C_{86}H_{94}O_{11}Si_2) + Na^+]$; 1H NMR (500 MHz) δ : 5.90 (d, 1H, $J_{1,2} = 3.5$ Hz, H-1); ^{13}C NMR δ : 138.99, 138.95, 138.7, 138.3, 138.04 and 137.96 (6 × C_{quat} . O-CH₂-Ph), 133.7, 133.4, 133.4, 133.1 (4 × C_{quat} . Si-Ph), 104.5 (C-2'), 89.6 (C-1), 84.3, 82.2, 82.1, 80.7, 80.5, 77.2, 71.6 (C-3', C-4', C-5', C-3, C-4, C-2, C-5), 75.7, 74.7, 73.5, 73.2, 72.6, 72.0, 71.8

(6 × O—CH₂—Ph, C-1'), 64.6, 62.3 (C-6, C6'), 27.0 and 26.6 [C(CH₃)₃], 19.3 and 19.2 [C(CH₃)₃].

Anal. calc. for: C₈₆H₉₄O₁₁Si₂ · H₂O: C, 74.97; H, 7.02; found: C, 75.10; H, 7.31%.

1,2,2',3,3',4,4'-Hexa-O-benzyl-6-O-(*tert*-butyldiphenylsilyl) sucrose (16)

Disilylated derivative **14** (2.84 g, 2.1 mmol) was dissolved in THF (20 mL), to which tetrabutylammonium fluoride trihydrate (1 g, 3.2 mmol) was added, and the mixture was stirred at rt for 36 h and partitioned between water (20 mL) and ethyl acetate (20 mL). The organic phase was separated and the aqueous one extracted with ethyl acetate (3 × 20 mL). Combined organic solutions were dried and concentrated, and the product was purified by column chromatography (hexane/ethyl acetate, 8:1) to afford **16** (having very different polarity than **15**, ΔR_f ~ 0.5) as a colorless oil (1.36 g, 1.2 mmol, 66%).

[α]_D = 29.8; *m/z* 1143.5105 calc. for [C₇₀H₇₆O₁₁NaSi (M+Na): 1143.5049]; ¹H NMR (500 MHz) δ: 5.57 (d, 1H, *J*_{1,2} = 3.4 Hz, H-1), 1.07 [s, 9H, C(CH₃)₃]; ¹³C NMR δ: 138.7, 138.5, 138.3, 138.25, 138.15, 137.8 (6 × C_{quat.} O—CH₂—Ph), 133.6 and 133.2 (2 × C_{quat.} Si—Ph), 103.9 (C-2'), 91.2 (C-1), 83.6, 81.7, 81.3, 80.0, 79.9, 77.2, 72.6, (C-3', C-4', C-5', C-3, C-4, C-2, C-5), 75.7, 75.0, 73.5, 73.2, 72.9, 72.5, 71.1 (6 × O—CH₂—Ph, C-1'), 62.0, 61.6 (C-6, C6'), 26.9 [C(CH₃)₃], 19.3 [C(CH₃)₃].

Anal. calc. for C₇₀H₇₆O₁₁Si: C, 74.97; H, 6.83; found: C, 74.94; H, 6.74%.

6-O-Mesyl-6'-O-(*tert*-butyl-diphenylsilyl)-1',2,3,3',4,4'-hexa-O-benzylsucrose (17)

To a cooled (to 0°C) solution of derivative **15** (1.08 g, 1 mmol) in dry methylene chloride (20 mL) containing DMAP (20 mg) and triethylamine (0.5 mL, 3.6 mmol), mesyl chloride (0.2 mL, 2.6 mmol) was added dropwise, and the mixture was stirred for 16 h at rt. Then water (20 mL) was added, the organic phase was separated, and the aqueous one extracted with ethyl acetate (3 × 20 mL). Combined organic solutions were dried and concentrated, and the product was purified by column chromatography (hexane/ethyl acetate, 5:1) to afford **17** as a colorless oil (1.01 g, 0.8 mmol, 87%).

[α]_D = 35.0; *m/z* 1221.4882 calc. for [C₇₁H₇₈O₁₃SiSnNa (M+Na): 1221.4825]; ¹H NMR (500 MHz) δ: 5.90 (d, 1H, *J*_{1,2} = 3.7 Hz, H-1), 4.08 (dt, 1H, *J*_{5,4} = 10.2 Hz, *J*_{5,6} = 2.4 Hz; H-5), 3.91 (d, 2H, H-6), 3.89 (dd, 1H, *J*_{3,2} = 9.4 Hz, *J*_{3,4} = 9.0 Hz, H-3), 3.47 (dd, 1H, H-4), 3.42 (dd, 1H, H-2), 2.68 (s, 3H, SO₂CH₃), 1.05 [s, 9H, C(CH₃)₃]; ¹³C NMR δ: 138.8, 138.3, 138.2 (double intensity), 137.9 and 137.8 (6 × C_{quat.} O—CH₂—Ph), 133.2 and 132.9 (2 × C_{quat.} Si—Ph), 104.3 (C-2'), 88.8, 84.0, 81.8, 81.0, 80.6, 79.9, 76.8, 68.9 (C-1, C-3', C-4', C-5', C-2, C-3, C-4,

C-5), 75.5, 74.8, 73.5, 73.4, 72.7, 72.1, 72.0, 68.3, 63.8 ($6 \times \text{O}-\text{CH}_2-\text{Ph}$, C-1', C-6, C6'), 36.9 (SO_2CH_3), 26.9 [$\text{C}(\text{CH}_3)_3$], 19.2 [$\text{C}(\text{CH}_3)_3$].

Anal. calc. for $\text{C}_{71}\text{H}_{78}\text{O}_{13}\text{SSi}$: C, 71.09; H, 6.55; S, 2.67; found: C, 70.98; H, 6.60; S, 2.80%.

6-O-(*tert*-Butyl-diphenylsilyl)-6'-O-mesyl-1',2,3,3',4,4'-hexa-O-benzylsucrose (18)

To a cooled (to 0°C) solution of derivative **16** (1.2 g, 1.1 mmol) in dry methylene chloride (20 mL) containing DMAP (cat.) and triethylamine (0.5 mL, 3.6 mmol), mesyl chloride (0.2 mL, 2.6 mmol) was added dropwise, and the mixture was stirred for 16 h at rt. Then water (20 mL) was added and reaction mixture was partitioned between two phases; the organic one was collected and the water one washed with ethyl acetate (3×20 mL). Combined organic phases were dried and concentrated. Product was purified by column chromatography (hexane/ethyl acetate, 5:1) to afford **18** as a colorless oil (1.2 g, 1.0 mmol, 93%).

$[\alpha]_{\text{D}} = 29.1$; m/z 1221.4725 calc. for $[\text{C}_{71}\text{H}_{78}\text{O}_{13}\text{NaSSi} (\text{M}+\text{Na}): 1221.4825]$; ^1H NMR (600 MHz) δ : 5.75 (d, 1H, $J_{1,2} = 3.0$ Hz, H-1), 2.76 [s, 3H, $\text{S}(\text{O})_2\text{CH}_3$]; ^{13}C NMR δ : 138.8, 138.6, 138.4, 137.74, 137.66, 137.6 ($6 \times \text{C}_{\text{quat.}} \text{O}-\text{CH}_2-\text{Ph}$), 133.5 and 133.3 ($2 \times \text{C}_{\text{quat.}} \text{Si}-\text{Ph}$), 105.0 (C-2'), 90.5 (C-1), 83.9, 82.0, 81.9, 80.1, 78.2, 77.3, 72.0 (C-3', C-4', C-5', C-3, C-4, C-2, C-5), 75.8, 74.9, 73.4, 73.1, 72.64, 72.59, 70.7, 69.9 ($6 \times \text{O}-\text{CH}_2-\text{Ph}$, C-1', C-6'), 62.6 (C-6), 37.3 [$\text{S}(\text{O})_2\text{CH}_3$].

Anal. calc. for $\text{C}_{71}\text{H}_{78}\text{O}_{13}\text{Si} \cdot \text{H}_2\text{O}$: C, 70.04; H, 6.62; found: C, 70.16; H, 6.37%.

6-Iodo-6-deoxy-6'-O-(*tert*-butyl-diphenylsilyl)-1',2,3,3',4,4'-hexa-O-benzylsucrose (19)

To a solution of derivative **17** (0.79 g, 0.66 mmol) in DMF (10 mL), KI (2 g) was added, and the mixture was stirred at 120°C for 72 h. Then it was cooled to rt and partitioned between water (10 mL) and diethyl ether (20 mL). The organic phase was separated and the aqueous one extracted with ether (3×40 mL). Combined organic solutions were dried and concentrated, and the product was purified by column chromatography (hexane/ethyl acetate, 6:1) to afford **19** as a colorless oil (0.72 g, 0.58 mol, 89%).

$[\alpha]_{\text{D}} = 30.4$; m/z 1253.4064 calc. for $[\text{C}_{70}\text{H}_{75}\text{O}_{10}\text{NaSiI} (\text{M}+\text{Na}): 1253.4066]$; ^1H NMR (500 MHz) δ : 5.83 (d, 1H, $J = 3.4$ Hz, H-1); ^{13}C NMR δ : 138.8, 138.7, 138.4, 138.2 and 137.9 double intensity ($6 \times \text{C}_{\text{quat.}} \text{O}-\text{CH}_2-\text{Ph}$), 133.3 and 132.9 ($2 \times \text{C}_{\text{quat.}} \text{Si}-\text{Ph}$), 104.2 (C-2'), 88.8, 83.9, 81.54, 81.51, 80.9, 80.6, 80.2, 68.4 (C-1, C-3', C-4', C-5', C-2, C-3, C-4, C-5), 75.5, 75.0, 73.5, 73.4, 72.6, 72.1 double intensity and 63.8 ($6 \times \text{O}-\text{CH}_2-\text{Ph}$, C-1', C-6'), 27.0 [$\text{C}(\text{CH}_3)_3$], 19.2 [$\text{C}(\text{CH}_3)_3$], 10.3 (C-6).

Anal. calc. for $C_{70}H_{75}IO_{10}Si$: C, 68.28; H, 6.14; I, 10.31; found: C, 68.42; H, 6.37; I, 10.36%.

6-O-(*tert*-Butyl-diphenylsilyl)-6'-deoxy-6'-iodo-1',2,3,3',4,4'-hexa-O-benzylsucrose (20)

To a solution of derivative **18** (1.07 g, 0.9 mmol) in DMF (10 mL), KI (3 g) was added, and the mixture was stirred at 120°C for 72 h. Then it was cooled to rt and partitioned between water (10 mL) and diethyl ether (20 mL). The organic phase was separated and the aqueous one extracted with ether (3 × 40 mL). Combined organic solutions were dried and concentrated, and the product was purified by column chromatography (hexane/ethyl acetate, 6:1) to afford **20** as a colorless oil (0.48 g, 0.4 mmol, 44%).

$[\alpha]_D = 21.5$; m/z 1253.4025 calc. for $[C_{70}H_{75}O_{10}NaSiI(M+Na): 1253.4066]$; 1H NMR (600 MHz) δ : 5.64 (d, 1H, $J_{1,2} = 3.5$ Hz, H-1), 1.07 [s, 9H, $C(CH_3)_3$]; ^{13}C NMR δ : 138.79, 138.75, 138.4, 138.0, 137.9, 137.8 ($6 \times C_{quat. O-CH_2-Ph}$), 133.6 and 133.3 ($2 \times C_{quat. Si-Ph}$), 104.8 (C-2'), 90.3 (C-1), 85.3, 84.5, 81.9, 80.4, 80.3, 77.4, 72.0 (C-3', C-4', C-5', C-3, C-4, C-2, C-5), 75.7, 74.9, 73.3, 72.83, 72.76, 72.4, 71.1, 62.6 ($6 \times O-CH_2-Ph$, C-1', C-6), 26.9 [$C(CH_3)_3$], 19.3 [$C(CH_3)_3$], 6.4 (C-6').

Anal. calc. for $C_{70}H_{75}IO_{10}Si$: C, 68.28; H, 6.14; found: C, 68.39; H, 6.05%.

6-(Diethoxy-phosphoryl)-6'-deoxy-6'-O-(*tert*-butyl-diphenylsilyl)-1',2,3,3',4,4'-hexa-O-benzylsucrose (21)

Compound **19** (0.59 g, 0.48 mmol) was dissolved in $P(OEt)_3$ (5 mL) and stirred and boiled under reflux in the oxygen-free atmosphere for 72 h. Excess of $P(OEt)_3$ was evaporated (below 70°C) and the product was purified by column chromatography (hexane/ethyl acetate, 3:1) to afford **21** as a colorless oil (0.51 g, 0.41 mmol, 86%).

$[\alpha]_D = 24.3$; m/z 1263.5396 calc. for $[C_{74}H_{85}O_{13}NaSiP (M+Na): 1263.5389]$; 1H NMR (500 MHz) δ : 5.67 (d, 1H, $J_{1,2} = 3.6$ Hz; H-1), 3.82–3.92 (m, 4H, $P-O-CH_2-CH_3$); ^{31}P NMR δ : 29.91; ^{13}C NMR δ : 138.8, 138.7, 138.42, 138.40, 138.21 and 138.18 ($6 \times C_{quat. O-CH_2-Ph}$), 133.5 and 133.3 ($2 \times C_{quat. Si-Ph}$), 105.0 (C-2'), 90.5 (C-1), 84.5, 83.7 and 81.9, 66.8 (d, $J_{CP} = 7.4$ Hz) (C-3', C-4', C-5, C-5'), 81.7 (C-3), 80.9 (d, $J_{CP} = 9.1$ Hz; C-4), 80.1 (C-2), 75.3, 74.7, 73.4, 73.2, 72.4, 72.2, 70.5 ($6 \times O-CH_2-Ph$, C-1'), 66.0, 61.3 (d, $J_{CP} = 6.1$ Hz), 61.2 (d, $J_{CP} = 6.2$ Hz) ($2 \times P-O-CH_2-CH_3$, C-6, C-6'), 28.5 (d, $J_{CP} = 98.7$ Hz) and 23.4 (d, $J_{CP} = 99.2$ Hz; $2 \times P-O-CH_2-CH_3$), 26.9 [$C(CH_3)_3$], 19.2 [$C(CH_3)_3$].

Anal. calc. for $C_{74}H_{85}O_{13}Psi \cdot H_2O$: C, 70.56; H, 6.96; found: C, 70.13; H, 7.33%.

1,2,2',3,3',4,4'-Hexa-O-benzyl-6-deoxy-6-(diethoxyphosphonate) sucrose (21a)

Compound **21** (245 mg, 0.20 mmol) was dissolved in THF (5 mL) containing tetrabutylammonium fluoride trihydrate (75 mg, 0.24 mmol), and the mixture was stirred at 60°C for 6 h, cooled to rt, and concentrated. Column chromatography (hexane/ethyl acetate, 3:1 to 1:1) afforded **21a** (146 mg, 0.14 mmol, 74%) as a colorless oil.

$[\alpha]_D = 29.7$ ($c = 0.35$); m/z 1025.4160 calc. for $[C_{58}H_{67}O_{13}NaP (M+Na): 1025.4212]$; 1H NMR (500 MHz) δ : 5.59 (d, 1H, $J_{1,2} = 3.4$ Hz, H-1); ^{31}P NMR δ : 29.89; ^{13}C NMR δ : 138.7, 138.6, 138.4, 138.3, 138.1 and 137.7 ($6 \times C_{quat}$. O-CH₂-Ph), 104.2 (C-2'), 90.8 (C-1), 84.4, 81.5, 81.4, 81.3, 81.2, 79.9 and 67.2 (d, $J_{CP} = 6.6$ Hz) (C-3', C-4', C-5', C-3, C-4, C-2, C-5), 75.3, 74.8, 73.5, 72.9, 72.7, 72.5, 70.5, 62.3, 61.6 (m) ($6 \times$ O-CH₂-Ph, C-1', C-6, C-6', $2 \times$ P-O-CH₂-CH₃), 16.4 (m) ($2 \times$ P-O-CH₂-CH₃).

Anal. calc. for $C_{58}H_{67}O_{13}P \cdot 2H_2O$: C, 67.01; H, 6.89; found: C, 66.75; H, 6.88%.

6'-(Diethoxy-phosphoryl)-6'-deoxy-6-O-(tert-butylidiphenylsilyl)-1',2,3,3',4,4'-hexa-O-benzylsucrose (22)

Compound **20** (0.40 g, 0.32 mmol) was dissolved in P(OEt)₃ (5 mL) and stirred at 120°C in the oxygen-free atmosphere for 72 h. The excess of P(OEt)₃ was evaporated (below 70°C) and the product was purified by column chromatography (hexane/ethyl acetate, 3:1) to afford **22** as a colorless oil (0.18 g, 0.14 mmol, 45%).

$[\alpha]_D = 28.2$; m/z 1263.5441 calc. for $[C_{74}H_{85}O_{13}NaSiP (M+Na): 1263.5389]$; 1H NMR (500 MHz) δ : 5.68 (d, 1H, $J_{1,2} = 3.3$ Hz, H-1); ^{31}P NMR δ : 28.9; ^{13}C NMR δ : 138.9, 138.8, 138.4, 138.10, 138.06, 138.0 ($6 \times C_{quat}$. O-CH₂-Ph), 133.6 and 133.3 ($2 \times C_{quat}$. Si-Ph), 104.9 (C-2'), 90.0 (C-1), 85.6 (d, $J_{CP} = 12.5$ Hz), 83.7, 82.1, 80.3, 77.4, 75.5, 71.9 (C-3', C-4', C-5', C-3, C-4, C-2, C-5), 75.7, 74.8, 73.4, 72.8, 72.5, 72.3, 71.6, 62.6, 61.7 (d, $J_{CP} = 6.1$ Hz), 61.4 (d, $J_{CP} = 5.6$ Hz) ($6 \times$ O-CH₂-Ph, C-1', C-6', C-6, $2 \times$ P-O-CH₂-CH₃), 26.9 [$C(CH_3)_3$], 19.3 [$C(CH_3)_3$], 16.4 (m) ($2 \times$ P-O-CH₂-CH₃).

Anal. calc. for $C_{74}H_{85}O_{13}SiP \cdot 2H_2O$: C, 69.57; H, 7.02; found: C, 69.38; H, 7.02%.

1,2,2',3,3',4,4'-Hexa-O-benzyl-6'-deoxy-6'-(diethoxyphosphonate) sucrose (22a)

Compound **22** (140 mg, 0.11 mmol) was treated analogously (to **21**) with tetrabutylammonium fluoride trihydrate without any result. We could observe

formation of **22a** only with tetrabutylammonium fluoride trihydrate in the presence of KOH and methanol, but the product was formed in very small amounts detectable by ms: m/z 1025 [$M(C_{78}H_{76}O_9P_2)+Na^+$].

6,6'-bis-(Diphenylphosphino)-6,6'-dideoxy-1',2,3,3',4,4'-hexa-O-benzylsucrose (**23**)

To a solution of triphenyl phosphine (0.86 g, 3.3 mmol) in dry THF (25 mL), metallic sodium (0.15 g, 6.5 mmol) was added in small pieces and the mixture was stirred at rt for 24 h under oxygen-free atmosphere (colorless solution became deep red). Such deeply red solution of phosphide was transferred via syringe into the solution of the dichloride derivative **9** (1 g, 1.1 mmol) in THF (5 mL) under oxygen-free atmosphere and the mixture was stirred at rt for 48 h (discoloration of the mixture). The residue was partitioned between water (15 mL) and toluene (15 mL), the organic phase was separated, and the aqueous one was extracted with toluene (3 × 30 mL). Combined organic solutions were dried and concentrated, and the residue was purified by column chromatography (hexane/ethyl acetate, 4:1 to 3:1) to afford **23** (0.39 g, 0.32 mmol, 29%) as a colorless oil.

Significant amounts of the di-oxide **24** were also isolated (hexane-ethyl acetate, 2:1 to 1:1).

Data for **23**: m/z 1219 [$M(C_{78}H_{76}O_9P_2)+H^+$]; 1H NMR (400 MHz) δ : 5.51 (d, 1H, $J_{1,2} = 3.3$ Hz, H-1); ^{31}P NMR δ : -22.1, -24.8; ^{13}C NMR δ : 138.8, 138.7, 138.5, 138.4, 138.3, 138.1 (6 × C_{quat.} O-CH₂-Ph), 104.4 (C-2'), 89.6, 86.6 (m), 84.2, 82.8 (d, $J_{CP} = 9.4$ Hz), 81.7, 80.2 and 78.6 (d, $J_{CP} = 16.3$ Hz) (C-1, C-3', C-4', C-5', C-2, C-3, C-4), 75.4, 74.9, 73.2, 72.5 (m), 72.4, 71.4 and 65.8 (C-1', 6 × O-CH₂-Ph), 69.4 (d, $J_{CP} = 13.7$ Hz, C-5), 34.2 (m) and 32.4 (d, $J_{CP} = 14.6$ Hz, C-6' and C-6).

Data for **24**: $[\alpha]_D = 3.6$; m/z 1273.4728 calc. for $[C_{78}H_{76}O_{11}NaP_2 (M+Na): 1273.4755]$ 1H NMR (400 MHz) δ : 5.04 (d, 1H, $J_{1,2} = 3.3$ Hz, H-1); ^{31}P NMR δ : 29.27, 28.0; ^{13}C NMR δ : 138.60 double intensity, 138.57, 138.4, 138.2, 138.0 (6 × C_{quat.} O-CH₂-Ph), 105.1 (C-2'), 89.9, 85.9 (d, $J_{CP} = 8.6$ Hz), 83.8, 81.9 (d, $J_{CP} = 9.4$ Hz), 81.3, 79.9 and 75.7 (d, $J_{CP} = 2.5$ Hz) (C-1, C-3', C-4', C-5', C-2, C-3, C-4), 75.2, 74.7, 73.3, 72.4, 72.3, 72.1 and 70.7 (6 × O-CH₂-Ph, C-1'), 67.0 (d, $J_{CP} = 5.1$ Hz, C-5), 35.3 (d, $J_{CP} = 69.4$ Hz) and 32.0 (d, $J_{CP} = 72.8$ Hz, C-6', C-6).

Anal. calc. for $C_{78}H_{76}O_{11}P_2$: C, 74.86; H, 6.12; found: C, 74.88; H, 6.14%.

The di-oxide **24** was converted into di-phosphine **23** by reduction with LAH. Thus, derivative **24** (185 mg, 0.15 mmol) was dissolved in THF (5 mL) containing methyl iodide (0.03 mL, 0.48 mmol) and the mixture was stirred under oxygen-free atmosphere at rt for 10 min. LAH (45 mg, 1.2 mmol) was added and stirring was prolonged for another 24 h. Methanol (1 mL) was added and the mixture was partitioned between water (10 mL) and ethyl acetate (20 mL).

The organic phase was separated and the aqueous one extracted with ethyl acetate (2 × 20 mL). Combined organic solutions were dried and concentrated, and the product was isolated by column chromatography (hexane/ethyl acetate, 4:1 to 3:1) to afford **23** as a colorless foam (88 mg, 0.07 mmol, 49%).

6,6'-bis-(Diphenylphosphinyl)-6,6'-dideoxy-1',2,3,3',4,4'-hexa-O-benzyl-sucrose (**24**)

A mixture of **23** and **24** (isolated from the preparation of phosphine **23** from **9**; 0.2 g, 0.22 mmol) was dissolved in acetone (3 mL), to which hydrogen peroxide (30% in water, 0.2 mL) was added, and the mixture was stirred for 24 h at rt. Then it was partitioned between water (5 mL) and ethyl acetate (15 mL). The organic phase was separated and the aqueous one extracted with ethyl acetate (3 × 15 mL). Combined organic solutions were dried and concentrated to afford title **24** in quantitative yield identical in all respects with the previously prepared sample.

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REFERENCES AND NOTES

1. See for example: Khan, R. The chemistry of sucrose. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 235–294; Hough, L. Selective substitution of hydroxyl groups in sucrose. In *Sucrochemistry*; ACS Symposium Series; Hickson, J.L., Ed.; ACS: Washington DC, 1977; vol. 41, 9–21; Khan, R. Chemistry and new uses of sucrose: how important? *Pure App. Chem.* **1984**, *56*, 833–844; Lichtenthaler, F.W. *Carbohydrates as Organic Raw Materials*, VCH: Weinheim, 1991; Vol. 1.; Descotes, G. *Carbohydrates as Organic Raw Materials*, VCH: Weinheim, 1993; Vol. 2; Mathlouthi, M.; Reiser, P. *Sucrose: Properties and Applications*; Blackie: Glasgow, 1995; Immel, S.; Lichtenthaler, F.W. Molecular modeling of saccharides, 7. The conformation of sucrose in water: a molecular dynamics approach. *Liebigs Ann. Chem.* **1995**, *11*, 1925–1937; Queneau, Y.; Fitremann, J.; Trombotto, S. The chemistry of unprotected sucrose: the selectivity issue. *C. R. Chimie* **2004**, *7*, 177–188.
2. Mach, M.; Jarosz, S.; Listkowski, A. Crown ether analogs from sucrose. *J. Carbohydr. Chem.* **2001**, *20*, 485–493; Review: Jarosz, S.; Mach, M. Regio- and stereoselective transformations of sucrose at the terminal positions. *Eur. J. Org. Chem.* **2002**, 769–780.
3. Queneau, Y.; Jarosz, S.; Lewandowski, B.; Fitremann, J. Sucrose chemistry and applications of sucrochemicals. *Adv. Carbohydr. Chem. Biochem.* **2007**, *61*, 217–292 and references therein.

4. Purves, C.B.; Hudson, C.S. The analysis of gamma-methylfructoside mixtures by means of invertase. IV. Behavior of sucrose in methyl alcohol containing hydrogen chloride. *J. Am. Chem. Soc.*, **1934**, *56*, 1973.
5. Hough, L.; Mufti, K.S.; Khan, R. Sucrochemistry: Part II. 6,6'-Di-*O*-tritylsucrose. *Carbohydr. Res.* **1972**, *21*, 144–147.
6. Franke, F.; Guthrie, R.D. *t*-Butyldimethylsilyl ethers of sucrose. *Austr. J. Chem.* **1977**, *30*, 639–647; *ibid.*, item. 6,6'-Di-*O*-*t*-butyldimethylsilylsucrose: studies on the rearrangements accompanying deblocking of such silyl ethers. *Austr. J. Chem.* **1978**, *31*, 1285–1290.
7. Karl, H.; Lee, C.K.; Khan, R. Synthesis and reactions of *tert*-butyldiphenylsilyl ethers of sucrose. *Carbohydr. Res.* **1982**, *101*, 31–38.
8. Jarosz, S.; Listkowski, A.; Lewandowski, B.; Ciunik, Z.; Brzuszkiewicz, A. Macrocyclic receptors containing sucrose skeleton. *Tetrahedron* **2005**, *61*, 8485–8492; Jarosz, S.; Lewandowski, B. Synthesis and complexation properties towards the ammonium cation of aza-coronand analogues containing sucrose. *Carbohydr. Res.* **2008**, *343*, 965–969.
9. Lewandowski, B.; Jarosz, S. Chiral recognition of α -phenylethylamine by sucrose-based macrocyclic receptors. *Chem. Commun.* **2008**, 6399–6401.
10. Jarosz, S.; Listkowski, A. Synthesis of macrocyclic derivatives containing sucrose unit. *J. Carbohydr. Chem.* **2003**, *22*, 753–763.
11. Jarosz, S.; Lewandowski, B.; Listkowski, A. Sucrose analogs containing sulfur functionalities. *Phosphorus Silicon Sulfur* **2009**, *184*, 1285–1295.
12. See for example: Dieguez, M.; Pamies, O.; Claver, C. Ligands derived from carbohydrates for asymmetric catalysis. *Chem. Rev.* **2004**, *104*, 3189–3215.
13. Scherrmann, M.C.; Boutboul, A.; Estramareix, B.; Hoffmann, A.S.; Lubineau, A. Binding properties and esterase activity of monoclonal antibodies elicited against sucrose 6-heptylphosphonate. *Carbohydr. Res.* **2001**, *334*, 295–307.
14. Jarosz, S.; Listkowski, A. Towards C-2 symmetrical macrocycles with incorporated sucrose unit. *Can. J. Chem.* **2006**, *84*, 492–496.
15. Ashby, E.C.; Gurumurthy, R.; Riddlehuber, R.W. Investigation of the purity of alkali metal diphenylphosphides and their reactions with organic halides. Evidence for single electron transfer. *J. Org. Chem.* **1993**, *58*, 5832–5837.
16. Payne, N.C.; Stephan, D.W. Preparation and ^{31}P nuclear magnetic resonance studies of chiral phosphines. *Can. J. Chem.* **1980**, *58*, 15–21.
17. Otake, T. Studies of Tritylated Sucrose. I. Mono-*O*-tritylsucroses. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3199–3205; *ibid.* item., Studies on Tritylated Sucrose. II. Di-*O*-Tritylsucroses., 1972, *45*, 2895–2898; Hough, L.; Mufti, K.S.; Khan, R. Sucrochemistry: Part II. 6,6'-Di-*O*-tritylsucrose. *Carbohydr. Res.*, **1972**, *21*, 144–147.
18. Jarosz, S.; Mach, M.; Frelek, J. Synthesis and structural analysis of the higher analogs of sucrose. *J. Carbohydr. Chem.* **2000**, *19*, 693–715; Mach, M.; Jarosz, S. Reaction of sugar phosphonates with sucrose aldehydes. Synthesis of higher analogs of sucrose. *J. Carbohydr. Chem.* **2001**, *20*, 411–424.