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Structure and ^{29}Si NMR Spectroscopy of Chiral Tri- and Tetra-alkoxysilanes. Observation of Restricted Rotation of 1,2:4,5-Di-*O*-isopropylidene-β-D-fructopyranose

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A number of hindered, chiral alkyltrialkoxysilanes, tetraalkoxysilanes and chlorotrialkoxysilanes have been prepared, and studied. The X-ray structures of di(1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranos-3-*O*-yloxy)isobutyl(2-phenylethoxy)silane (**1**), di(1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranos-3-*O*-yloxy)(hexa-2,4-dienyloxy)vinylsilane (**3**) and (2-phenylethoxy)tri(1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranos-3-*O*-yloxy)silane (**6**) are reported. In all structures the 1,2:4,5-diisopropylidene-β-D-fructopyranose, one of the alkoxy-substituents, was found to have a fixed conformation about the O3–C3 bond with hydrogen and silicon being eclipsed.

Silyl ethers have found great utility in organic synthesis not only as protecting groups,[1a] but also as reagents in many different reactions.[1b] Particularly interesting is the use of silicon to tether reagents together to achieve various kinds of selectivity in organic synthesis.[2] However, it has been mainly monoalkoxysilanes that have been employed in the various applications, while dialkoxysilanes have been much less used, and tri- and tetra-alkoxysilanes not at all.

We have recently found that tri- and tetra-alkoxysilanes with somewhat hindered chiral groups are configurationally and hydrolytically stable compounds which can be purified by normal chromatographic techniques.[3] Only a handful of X-ray structures of alkyltrialkoxysilanes[4] and tetraalkoxysilanes[5] are known; these compounds are very simple and often cyclic compounds, i.e., derivatives of diols. In this paper we have studied the ^{29}Si NMR spectroscopy and X-ray structures of a number of these relatively stable tri- and tetra-alkoxysilanes to learn more about their structure.

Results and discussion

Compound synthesis. Compounds **2**, **6**, **7**, **8** and **10** were prepared as described previously.[3] The alkyltrialkoxysilanes **1** and **3** were obtained essentially by the method described for the synthesis of such compounds.[3] The alkyltrichlorosilanes were allowed to react with 2 equivalents of 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose in pyridine and toluene. When the reaction, as judged by TLC, was complete, the final alcohol was added, and the reaction was allowed to go to completion. Particularly noteworthy was the high yield of **3**, 78%, which was higher than those obtained previously[3] for compounds of type $RSiOR'(OR'')_2$. The yield of **1** was modest (30%) as some by-products were formed in the reaction.

Compound **4** was originally obtained in an attempt to prepare a chiral chlorosilane containing the 2,3-isopropylidene-1,1,4,4-tetra-*C*-phenyl-L-threitol moiety. Thus methyltrichlorosilane was reacted with 2,3-isopropylidene-1,1,4,4-tetra-*C*-phenyl-L-threitol in the presence of pyridine. According to TLC this resulted mainly in the formation of **4**, which could be isolated by chromatography in 65% yield. It was somewhat surprising that compound **4** was reproducibly obtained in good yield because no water had been added from which the OH could be formed. Regarding the origin of the water, the hydroxy group must be formed by hydrolysis of the chloride *after* the 2,3-isopropylidene-1,1,4,4-tetra-*C*-phenyl-L-threitol moiety has been introduced, because if $MeSiCl_2OH$ was formed, it would rapidly dimerise to $MeSiCl_2OSiMeCl_2$. If there were water present in the reaction medium it should, however, react much faster

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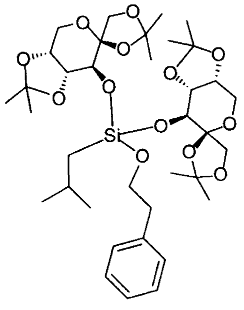
with chlorosilanes than the tertiary alcohol. It is thus not likely that a significant amount of water was present, which was also confirmed by the fact that no hydrolysis products were observed when the same set of reagents and solvents were used in other contexts. The most reasonable explanation for the formation of **4** is thus by hydrolysis of the corresponding chloride on the silica gel of both TLC plates and column.

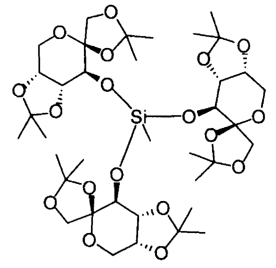
Even more pronounced hydrolysis of a chlorosilane on silica gel was observed in the reaction of tetrachlorosilane with 3 mol of 1,2:4,5-di-*O*-isopropylidene-β-D-fructose. After chromatographic purification the hydroxy compound **5** was obtained in 95% yield.

Determination of the structure of **4** and **5** need some comment. Differentiation between chloride and hydroxy compound by ^{1}H and ^{13}C NMR spectroscopy was not an easy matter as the chemical shift differences of the alkoxy groups were extremely small. However, both **4** and **5** gave satisfactory mass spectra showing the expected molecular ion peak, and in both cases an SiOH proton could be seen in the ^{1}H NMR spectrum.

It is known that some sterically hindered chlorosilanes are stable enough to allow them to be chromatographed.[6] These are typically silanes heavily substituted with *tert*-butyl or similar groups. However, we found that the trialkoxychlorosilanes **9** and **10**,[3] in complete contrast with the chemistry observed above, were stable enough to allow them to be chromatographed. Compound **9** was particularly stable. This compound could be obtained by chromatography as an oil, from which pure **9** was obtained crystalline in 40% yield by crystallisation in an open flask. No spontaneous hydrolysis occurred under these conditions. The compound, however, reacted readily with an alcohol in the presence of pyridine to yield the corresponding tetraalkoxysilane.[7] The ^{13}C NMR spectrum of **9** was identical with that of borneol,[8] to within 0.6 ppm, on all carbons except for a 2.1 ppm downfield shift of C-2. This downfield shift may be explained by the close proximity of the electronegative chlorine atom.


1

- 47.8 ppm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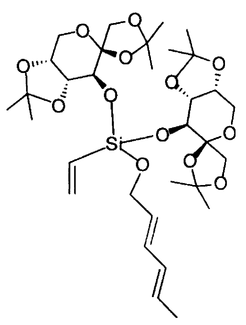
- 41.5 ppm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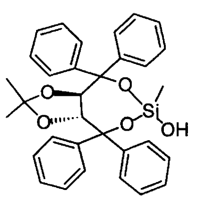
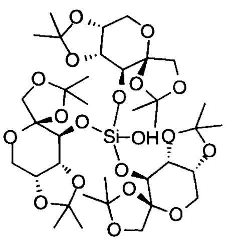
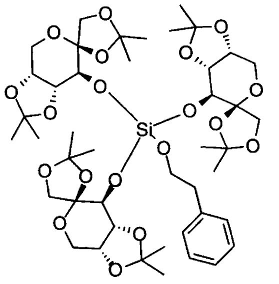

4

- 49.5 ppm

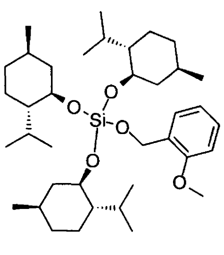
Fig. 1. Alkyltrialkoxysilanes and their ^{29}Si chemical shift.


5

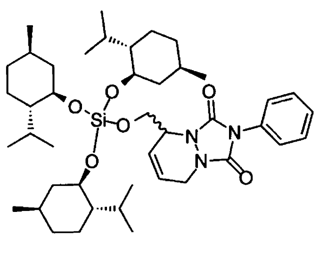
- 79.6 ppm


6

- 87.2 ppm


7

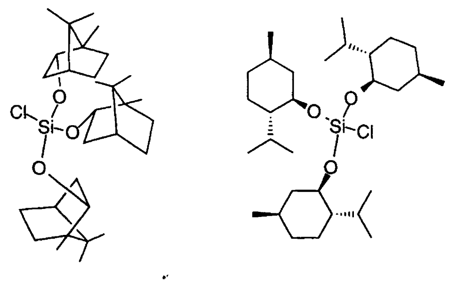
- 85.3 ppm


8

- 85.78 ppm
- 85.85 ppm

Fig. 2. Tetraalkoxysilanes and their ^{29}Si chemical shift.

^{29}Si NMR spectroscopy. While ^{1}H and ^{13}C NMR spectroscopy in general gave limited structural information about this type of compound, ^{29}Si NMR was expected to be more useful. Therefore the silicon chemical shifts of compounds **1**, **2** and **4**–**10** were measured relative to tetramethylsilane (TMS) (Figs. 1–3). All spectra were obtained for samples in solution except that of **4** which was obtained in solid state. The solid state ^{29}Si CP/MAS NMR spectrum showed a broad peak at −49.5 ppm with a linewidth of 240 Hz (4 ppm). The peak contained at least three different resonances suggesting possible different conformations in the solid state. The silicon nucleus is generally shielded by oxygen functionalities and deshielded by alkyl and halogen substituents.[9] Thus tetramethoxysilane has a chemical shift of δ −79.22 ppm relative to TMS. For the alkyltrialkoxysilanes **1**, **2** and **4** the deshielding effect of the single alkyl group was



9　　**10**

- 71.3 ppm　　- 74.6 ppm

Fig. 3. Chlorotrialkoxysilanes and their ^{29}Si chemical shift.

considerable. By comparison of **2** and **6** a deshielding effect of 45.7 ppm for methyl compared to phenethoxy was observed. This was a much larger effect than the substituent effect (24 ppm) observed between methyl and methoxy substituent in silatranes.[10]

The silicic acid derivatives **5**–**8** had chemical shifts in the expected upfield range of −75 to −90 ppm. Compound **8** was a mixture of diastereoisomers giving two peaks in the spectrum. Noteworthy was that replacement of the phenethoxy group of **6** with a hydroxy group in **5** resulted in a downfield shift of 7.6 ppm.

The shifts of the chloroalkoxysilanes were shifted upfield compared with the tetraalkoxysilanes. The substituent effect of chlorine in **10** compared with an alkoxy group in **7** or **8** was 11 ppm. This is very similar to the substituent effect between methoxy and chlorine (8.4 ppm) in silatranes.[10]

X-Ray structures. X-ray structures were obtained on compounds **1**, **3** and **6** (Figs. 4–6).

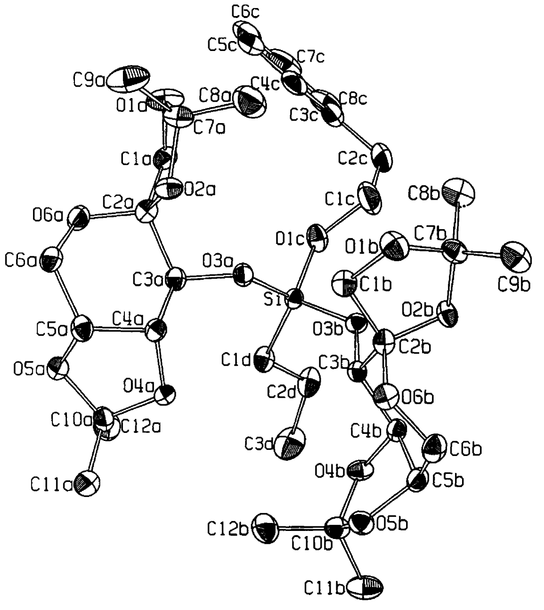


Fig. 4. X-Ray structure of **1**.

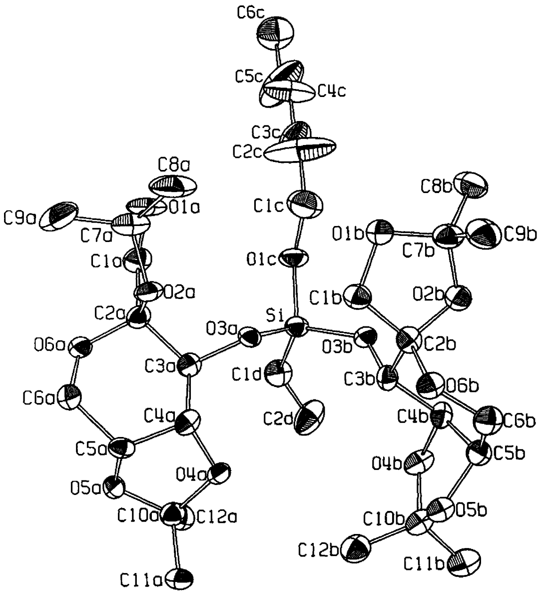


Fig. 5. X-Ray structure of **3**.

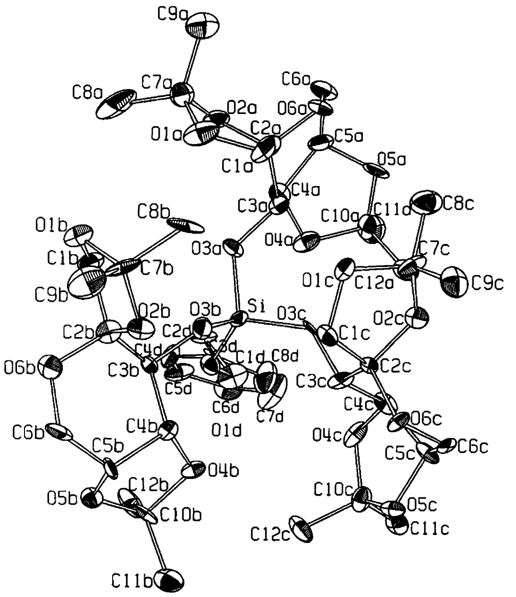


Fig. 6. X-Ray structure of **6**.

The structure of **1** (Fig. 4) has a somewhat disordered phenethoxy group. Only the main position (7%) is given. All the bonds to silicon have a typical bond length: the Si–O bonds were 1.631(3) Å, while the Si–C bond was 1.848(4) Å. The Si atom did not show a perfect tetrahedral symmetry as the two bond angles between the substituents were not 109.5° but varied between 105.6° and 113.5°. The largest angles, 113.5° and 112.4°, were between the isobutyl group and the two fructose groups, while the smallest angle, 106°, was between the two fructose units. This suggests that the most sterically demanding substituent is the isobutyl group, which primarily interacts with the fructose units pressing them together. The torsion angles (three-bond) between silicon and H-3 along the oxygen–carbon bond in each fructose were −12° and −1° showing that hydrogen and silicon were, in both cases, almost eclipsed. This conformation seems favorable because there is relatively little steric interaction between the bulky substituents on the fructose and the silicon substituents. The torsion angles along the fructose O–Si bonds were quite different, however, being −20° and −71° measured between isobutyl-C and C-3 of fructose.

The structure of **3** showed the hexadienyl moiety in an outstretched conformation pointing away from the silicon atom (Fig. 5). The Si–O bonds were 1.62–1.63 Å, while the Si–C bond was 1.83 Å. Again the angle between the substituents on silicon varied, in this case between 105.1 and −114.9°. The largest angles were between the vinyl C and the two fructose O, which were 114.9° and 112.1°, respectively. The smallest angles (105.1° and 106.2°, respectively) were observed between vinyl C and phenethoxy and between the fructose units. Again the torsion angles between silicon and H-3 in each fructose were close to zero: +10° and 2°. Similar to **1**, the torsion angles along the fructose O–Si bonds were quite different being −93° and −17° measured between vinyl-C and C-3 of fructose.

The structure of **6** also showed that all the bonds to silicon had the typical bond length (Fig. 6). Slight dissymmetry was observed in the Si–O bonds: while the Si–O bonds to the fructose moieties were 1.64–1.66 Å, the Si–O bond to the oxygen of phenethyl alcohol was only 1.61 Å. The two-bond angles from phenethyl oxygen to the fructose oxygens were 112.9°, 105.9° and 115.0°, respectively. The torsion angles between silicon and H-3 in each fructose were as in **1** and **3** close to zero: −10°, −25° and 6°. Thus only one fructose unit was somewhat twisted from a position in which Si and H-3 were eclipsed. The three torsion angles along the fructose O–Si bonds varied widely. Measured between phenethyl O and C-3 they were −123°, −6° and −64°.

All three structures had angles around the silicon atom (O–Si–O) averaging 109.4–109.5° with relatively small variations ($<6°$) suggesting tetrahedral geometry. One might reasonably assume that these variations were caused by lack of space for the bulky substituents, particularly the fructose units, in a perfect tetrahedron. However the O–Si–O angles between fructose units are, in all three structures, surprisingly among the smallest (average 106.9°). This suggests attraction between these groups, the opposite of what one might have expected. A reasonable explanation, at least for structures **1** and **3**, is that the alkyl subtituent is the more sterically demanding group close to silicon; apparently the fructose moieties are able to fulfill their steric demands through rotation.

Inspection of the torsion angles O–Si–O–C_3 and Si–O–C_3–H_3 in all three molecules revealed that while the former varied widely, the latter was surprisingly constant for seven different fructose moieties with an angle close to zero (average −1.9°). Thus the silicon and H_3 had a clear preference for being eclipsed. Rotation around the O–C_3 bond using molecular modelling revealed indeed that other conformations were sterically highly unfavorable because of interactions between the isopropylidene groups of fructose and the large silicon group. Thus a conformation of the diisopropylidene fructose units as shown in Fig. 7 seems dictated. Whether the same conformation prevails for other diisopropylidene fructose derivatives, such as esters, is presently not known as none have been subjected to X-ray structure determination according to the records of the Cambridge Crystallographic Database.

As mentioned above, the torsion angle O–Si–O–C_3 was highly variable and modelling confirmed that relatively little steric hindrance occurred when Si–O rotation was performed. This free Si–O rotation is probably responsible for the fact that even three fructosyl units can fit around the silicon atom without much distortion.

In summary, all three compounds had tetrahedral geometry at silicon with very small variations even though very bulky substituents were present, and it may be assumed that this is generally the case. No unusual geometrical features account for the relatively high stability of these molecules. This is probably caused simply by a higher degree of steric hindrance than occurs for simple alkoxysilanes. However some interesting information was obtained about the geometry of a silicon ether of diisopropylidenefructose. A wide variation of the torsion angles along the silicon–fructose–O3 bond suggests that relatively free rotation can occur along this bond. That was not the case for rotation along the O3–C3 bond. Torsion angles along that bond all indicated that a conformation with H3 and Si eclipsed was clearly preferred suggesting that the conformation shown in Fig. 7 is highly preferred.

Conclusion

From these observations it can be concluded that silyl groups with diisopropylidenefructose as alkoxy substituents are not ideal as chiral auxiliaries since the Si–O bond has rotational freedom resulting in stereoinduction being a sum of the induction of many different conformations. However many other chiral alkoxy substituents may possess rotational freedom not only along the Si–O bond but also along the O–C bond. Along the O–C bond, present observations suggest that the diisopropylidenefructose unit does not rotate and as such it has less conformational freedom than many other readily available chiral alkoxy groups. Thus it may be predicted that

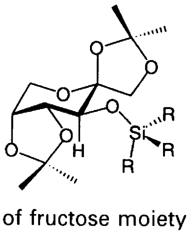


Fig. 7. Conformation of fructose moiety.

if Si–O bond rotation can be inhibited, e.g., by changing substituents on silicon, a much more promising chiral auxiliary or protecting group may result.

Experimental

General. ^{13}C NMR and ^{1}H NMR spectra were recorded on Varian 200 and 300 MHz Gemini instruments. When CDCl$_3$ was used as the solvent TMS and CDCl$_3$ (^{13}C NMR: δ 76.93 ppm) were used as references. ^{29}Si NMR spectra were recorded on a JEOL 200 MHz NMR spectrometer operating at 53.24 MHz. Samples were run in deuteriated THF with TMS as a reference (set at 0.0 ppm) and spectra were acquired in the NNE mode. Solid state ^{29}Si CP/MAS NMR spectra were recorded on a Varian Unity INOVA 300 S NMR spectrometer at 59.59 MHz using a home-built CP/MAS probe for 7 mm rotors. The ^{29}Si chemical shifts were measured relative to an external sample of TMS. Melting points are uncorrected. Optical rotations were measured on a Perkin Elmer 241 polarimeter. Solutions were concentrated on a rotary evaporator at temperatures below 40 °C.

*Di(1,2:4,5-diisopropylidenefructopyranos-3-*O*-yloxy)-isobutyl(2-phenylethoxy)silane* (**1**). To 1,2:4,5-diisopropylidenefructopyranose (522 mg, 2 mmol) and isobutyltrichlorosilane (192 mg, 1 mmol) in toluene (5 ml) was added pyridine (0.5 ml). The solution was stirred for 5 h at 20 °C. 2-Phenylethyl alcohol (122 mg, 1 mmol) was then added, and the mixture was stirred overnight. TLC showed **1** as the main product among several. Purification was performed by column chromatography [16 cm (h) × 2.5 cm (d)] eluting with Et$_2$O–pentane (1:3). The product could be recrystallized from MeCN. Yield: 215 mg (30%). $[\alpha]_{\text{D}}^{20}$ −120.7° (*c* 0.6, CHCl$_3$). ^{13}C NMR (CDCl$_3$): δ 138.8, 129.0 (2 C, Ph), 128.2 (2 C, Ph), 126.1 (Ph), 111.7, 111.6, 108.9, 108.8 (O–C–O), 104.93, 104.87 (C-2), 77.4, 77.3, 73.7, 71.9, 71.94, 71.87, 71.3 (C-3, C-4, C-5, C-6), 63.7 (CH$_2$O), 60.50, 60.46 (C-1), 38.9 (CH$_2$Ph), 28.1, 26.45, 26.41, 26.3, 26.2, 26.1, 25.9, 23.7, 21.2 (8 MeC, 2 MeCH, CH, CH$_2$Si). ^{1}H NMR (CDCl$_3$): δ 7.2 (5 H, m, Ph), 3.8–4.2 (16 H, m), 2.82 (2 H, t, CH$_2$Ph), 1.90 (1 H, m, CH), 1.2–1.6 (24 H, 8s, 8 MeC), 1.0 (6 H, 2 d, 2 MeCH), 0.8 (1 H, dd, SiCHH), 0.7 (1 H, dd, SiCHH). MS (EI): *m*/*z* 724 (M$^+$).

Di(1,2:4,5-diisopropylidenefructopyranos-3-oxy)(hexa-2,4-dienyloxy)vinylsilane (**3**). To 1,2:4,5-diisopropylidenefructopyranose (410 mg, 1.6 mmol) in toluene (20 ml) was added trichloro(vinyl)silane (0.100 ml) and pyridine (0.200 ml). The reaction was stirred overnight after which sorbyl alcohol (0.090 ml) was added. Three hours later the precipitate was removed by filtration, and the filtrate was evaporated. Column chromatography in diethyl ether–petroleum ether (1:4) gave 410 mg (78%) of **3**. M.p. 98–100 °C. $[\alpha]_{\text{D}}^{20}$ −134° (*c* 1.0, CHCl$_3$). ^{13}C NMR (CDCl$_3$): δ 137.64, 130.81, 130.76, 129.10, 129.00, 128.68 (CH=), 111.72, 108.88, 108.82 (O–C–O), 104.68 (C-2), 77.25, 77.11, 76.57, 73.67, 73.63, 71.65, 71.25, 71.11 (C-3, C-4, C-5, C-6), 63.33 (CH$_2$O), 60.28, 60.26 (C-2), 28.04, 28.01, 26.44, 26.21, 26.05 (MeC), 17.97 (MeCH). ^{1}H NMR (CDCl$_3$): δ 6.19–5.90 (5 H, m, CH=), 5.66–5.56 (2 H, m, CH$_2$=), 4.38–3.87 (16 H, m, CH–O and CH$_2$–O), 1.71 (3 H, d, MeCH), 1.51 (3 H, s, MeC), 1.47 (3 H, s, MeC), 1.45 (6 H, s, 2 MeC), 1.37 (3 H, s, MeC), 1.36 (3 H, s, MeC), 1.30 (3 H, s, MeC), 1.29 (3 H, s, MeC).

*2,3-*O*-Isopropylidene-1,4-*O*-(hydroxymethyl)silylene-1,1,4,4-tetra-*C*-phenyl-*L*-threitol* (**4**). To 2,3-*O*-isopropylidene-1,1,4,4-tetra-*C*-phenyl-L-threitol (263 mg, 0.56 mmol) and methyltrichlorosilane (85 mg, 0.56 mmol) in 15 ml of THF was added 0.5 ml of pyridine. The solution was stirred overnight at 20 °C. TLC showed the presence of 4, which was purified by column chromatography [15 cm (h) × 2.5 cm (d)] in Et$_2$O–pentane (1:4). A crystalline product was obtained (133 mg, 65%). The slower-moving fraction of unchanged 2,3-*O*-isopropylidene-1,1,4,4-tetra-*C*-phenyl-L-threitol (86 mg, 33%) was also obtained. M.p. 190–3 °C $[\alpha]_{\text{D}}^{20}$ −251.4 (*c* 0.5, CHCl$_3$). ^{13}C NMR (CDCl$_3$): δ 147.8, 147.5, 142.8, 142.7 (*ipso*-C), 129.5, 129.3, 128.8, 128.5, 128.0, 127.9, 127.4, 127.3 (*o*, *m* and *p*-C), 114.3 (O–C–O), 82.7 (2 C–O), 81.9, 81.8 (2 CH–O), 27.5, 27.4 (Me$_2$C), −3.6 (MeSi). ^{1}H NMR (CDCl$_3$): δ 7.75–7.15 (20 H, m, Ph), 5.1 (2 H, 2 d, CH–O), 2.05 (1 H, OH), 0.5–0.6 (6 H, 2 s, Me$_2$C), 0.1 (3 H, s, MeSi). MS (EI): *m*/*z* 524 (*M*$^+$).

*Tri(1,2:4,5-diisopropylidenefructopyranos-3-*O*-yloxy)-hydroxysilane* (**5**). To 1,2:4,5-diisopropylidenefructopyranose (3.44 g, 13.2 mmol) and SiCl$_4$ (0.50 ml, 4.4 mmol) in toluene (50 ml) was added pyridine (5 ml). The solution was stirred for 2 h at 45 °C, after which it was filtered through a silica pad [0.5 cm (h) × 3 cm (d)] using Et$_2$O–pentane (2:1). Evaporation of the filtrate gave an oil that was crystallised from Et$_2$O–pentane. Yield: 3.44 g (95%). ^{13}C NMR (CDCl$_3$): δ 112.55, 109.69 (2 O–C–O), 105.07 (C-2), 77.98, 74.29, 72.08, 71.86 (C-3, C-4, C-5, C-6), 60.63 (C-1), 28.6, 27.35, 26.58, 26.45 (4 Me). ^{1}H NMR (CDCl$_3$): δ 3.9–4.3 (21 H, m, CH and CH$_2$), 1.3–1.6 (36 H, m, Me). MS (EI): *m*/*z* 822 (*M*$^+$).

X-Ray crystal structures. Data collection, processing, structure analysis and refinement were carried out as described in Ref. 11.

Crystal data **1**. C$_{36}$H$_{56}$O$_{13}$Si, *M* 710.91. Monoclinic, $a = 11.681(2)$, $b = 10.102(2)$, $c = 16.542(3)$. $\beta = 105.03(1)°$, $V = 1885(1)$ Å^3 (by least-squares refinement on diffractometer angles for 40 automatically centred reflections, λ 0.71073), space group $P2_1$. White.

Crystal data **3**. C$_{32}$H$_{50}$O$_{13}$Si, *M* 673.78. Orthorhombic, $a = 10.1427(2)$, $b = 12.3546(3)$, $c = 28.5178(4)$. $V = 3573.54$ Å^3 (as above), space group $P2_1\,2_1\,2_1$. White.

Crystal data **6**. $C_{44}H_{66}O_{19}Si$, *M* 927.10. Monoclinic, $a=17.86(5)$, $b=10.09(5)$, $c=13.64(5)$. $\beta=98.14°$, $V=2433(16)$ Å^3 (as above), space group $P2_1$. White.

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