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Note

Crystal and molecular structure of 5-azido-3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose*

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Several mono- and bi-cyclic polyhydroxylated alkaloids, isolated from plants[2], are specific and potent glycosidase inhibitors[3], including those involved in the processing of glycoproteins[4]. Convenient intermediates for the synthesis of these compounds are 5-azido-5-deoxy sugar derivatives.

Attempts to synthesise 5-azido-5-deoxy derivatives of D sugars by treatment of 6-*O*-acetyl-3-*O*-benzoyl-5-chloro-5-deoxy-1,2-*O*-isopropylidene-β-L-ido-[5] or -talo-furanose[1] with potassium azide in *N*,*N*-dimethylformamide at ~95° resulted in considerable decomposition. As bromide is a better leaving group, an attempt was made to use the corresponding 5-bromide. However, treatment of 3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-5-*O*-mesyl-α-D-allofuranose (**2**), obtained by mesylation of **1**, with potassium bromide in *N*,*N*-dimethylformamide at ~90° for 7 days gave two C-5-epimeric bromides (**3** and **4**) in the ratio 1.6:1.

The ^{13}C-n.m.r. spectra of **3** and **4**, which were nearly identical, clearly showed a downfield shift of the C-5 resonance by ~18 p.p.m. compared to that of the 5-hydroxy derivative[1] (δ 53.7 for **3** and 53.2 for **4**). The ^{1}H-n.m.r. spectra of **3** and **4** agreed well with the proposed structure. The $J_{4,5}$ values of 4.2 and ~0 Hz for **4** and **3**, respectively, are consistent with the D-*allo* and L-*talo* configurations[6], respectively.

It is likely that the formation of the epimers **3** and **4** is due to the combined effects of the drastic reaction conditions and steric hindrance by the *tert*-butyldiphenylsilyl group. Bromides epimeric at C-5 were also obtained in the ratio ~1.4:1 when the corresponding 6-benzoate was treated as above for **2**; the bromides could not be separated, but their ^{13}C-n.m.r. spectra contained signals for C-5 at δ 49.9 and 49.6. The bromide **4** was synthesised conveniently by the reaction of 3,5-*O*-benzylidene-6-*O*-*tert*-butyldiphenylsilyl-1,2-*O*-isopropylidene-α-D-glucofuranose with *N*-bromosuccinimide, followed by Zemplén debenzoylation, an oxidation–reduction sequence, and benzoylation[7].

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[*] 5-Azido-5-deoxy-L-talofuranose Derivatives, Part. 3. For Part 2, see ref. 1.

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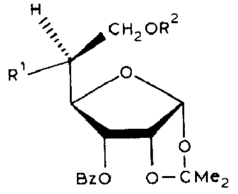
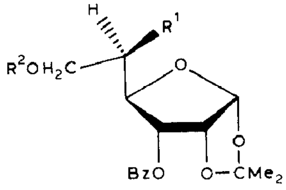


1 $R^1 = OH, R^2 = {}^tBuPh_2Si$
2 $R^1 = OMs, R^2 = {}^tBuPh_2Si$
4 $R^1 = Br, R^2 = {}^tBuPh_2Si$
5 $R^1 = N_3, R^2 = {}^tBuPh_2Si$



3 $R^1 = Br, R^2 = {}^tBuPh_2Si$
6 $R^1 = N_3, R^2 = {}^tBuPh_2Si$

The bromides **3** and **4** each reacted with potassium azide in *N*,*N*-dimethylformamide to give the 5-azido-5-deoxy derivatives **5** and **6**, respectively. The ^{1}H-n.m.r. spectrum of **5** was poorly resolved, but that for **6** showed a $J_{4,5}$ value of 2.6 Hz, consistent with the L-*talo* configuration[6]. The structure of **6** was confirmed by X-ray crystallography.

The structure of **6** and the numbering system are shown in Fig. 1, and the bond lengths and bond angles are given in Tables I and II, respectively. The unit cell contains discrete molecules of **6** (Fig. 2), a single molecule comprising the asymmetric unit. Torsion angles for the two rings in the molecule are shown in Table III. Unlike 1,2-*O*-isopropylidene-α-D-glucofuranose[8] or 5-azido-5-deoxy-*N*,*N*-diethyl-1,2-*O*-isopropylidene-3-*O*-mesyl-β-L-idofuranuronamide[9], the crystal structure of **6** revealed only one asymmetric molecule. The furanose ring is close to the $^3T_4$ conformation (φ = 116°, Q = 34 pm). However, the $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ values of 3.7, 4.9, and 8.4 Hz, respectively, in its ^{1}H-n.m.r. spectrum are consistent with the $^3T_2$ conformation, which is that normally found in many 1,2-*O*-isopropylidene and 1,2-*O*-ethylidene furanoid derivatives in solution[10]. The dioxolane (isopropylidene) ring also has a twist ($^2T_1$)

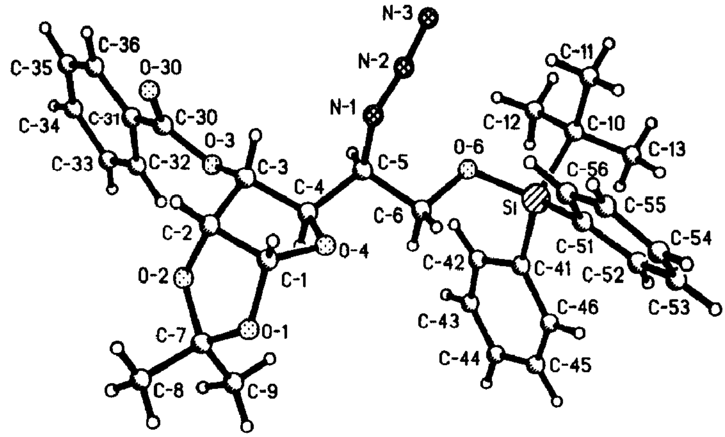


Fig. 1. Numbering system used for 5-azido-3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose (**6**)

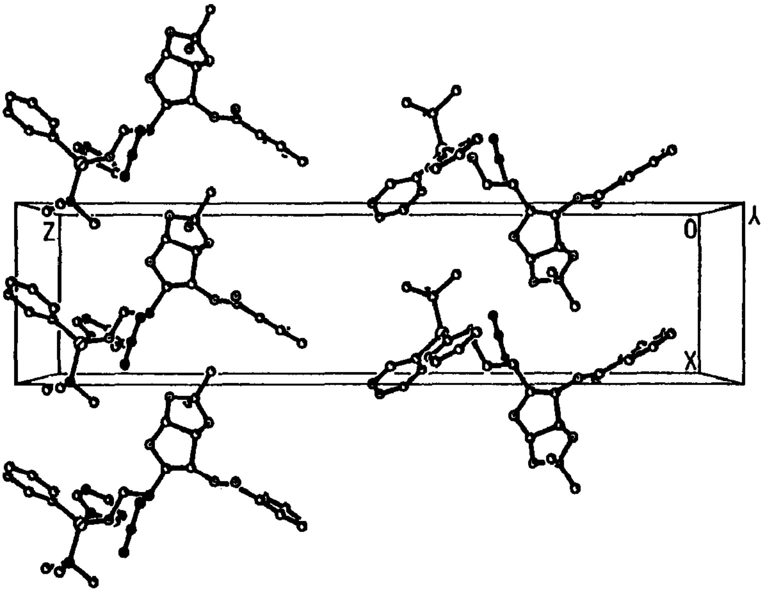


Fig. 2. Molecular packing in 5-azido-3-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose (**6**)

TABLE I

Bond lengths (Å) for **6**

Si–O-6	1.669 (7)	Si–C-10	1.869 (13)
Si–C-41	1.857 (12)	Si–C-51	1.864 (12)
O-1–C-1	1.363 (13)	O-1–C-7	1.439 (15)
O-2–C-2	1.386 (13)	O-2–C-7	1.425 (14)
O-3–C-3	1.413 (12)	O-3–C-30	1.312 (13)
O-4–C-1	1.411 (13)	O-4–C-4	1.437 (12)
O-6–C-6	1.420 (13)	O-30–C-30	1.267 (15)
N-1–N-2	1.238 (16)	N-1–C-5	1.435 (15)
N-2–N-3	1.148 (17)	C-1–C-2	1.534 (14)
C-2–C-3	1.510 (15)	C-3–C-4	1.495 (14)
C-4–C-5	1.509 (14)	C-5–C-6	1.502 (14)
C-7–C-8	1.489 (16)	C-7–C-9	1.509 (18)
C-10–C-11	1.451 (19)	C-10–C-12	1.558 (19)
C-10–C-13	1.548 (18)	C-30–C-31	1.427 (16)
C-31–C-32	1.454 (18)	C-31–C-36	1.368 (17)
C-32–C-33	1.370 (17)	C-33–C-34	1.403 (21)
C-34–C-35	1.328 (28)	C-35–C-36	1.382 (20)
C-41–C-42	1.417 (19)	C-41–C-46	1.390 (18)
C-42–C-43	1.354 (24)	C-43–C-44	1.326 (25)
C-44–C-45	1.349 (25)	C-45–C-46	1.346 (22)
C-51–C-52	1.403 (17)	C-51–C-56	1.372 (18)
C-52–C-53	1.380 (20)	C-53–C-54	1.374 (26)
C-54–C-55	1.337 (25)	C-55–C-56	1.402 (21)

TABLE II

Bond angles (°) for **6**

O-6–Si–C-10	104.9(5)	O-6–Si–C-41	107.9(5)
O-10–Si–C-41	113.7(6)	O-6–Si–C-51	107.3(5)
C-10–Si–C-51	108.9(5)	O-41–Si–C-51	113.6(5)
C-1–O-1–C-7	110.9(8)	C-2–O-2–C-7	111.2(8)
C-3–O-3–C-30	119.4(8)	C-1–O-4–C-4	111.2(7)
Si–O-6–C-6	121.2(6)	N-2–N-1–C-5	117.5(10)
N-1–N-2–N-3	170.8(13)	O-1–C-1–O-4	116.3(9)
O-1–C-1–C-2	103.9(8)	O-4–C-1–C-2	106.2(8)
O-2–C-2–C-1	103.4(8)	O-2–C-2–C-3	109.3(8)
C-1–C-2–C-3	103.0(8)	O-3–C-3–C-2	114.6(8)
O-3–C-3–C-4	112.0(8)	C-2–C-3–C-4	103.9(8)
O-4–C-4–C-3	103.4(8)	O-4–C-4–C-5	108.4(8)
C-3–C-4–C-5	117.4(9)	N-1–C-5–C-4	109.2(9)
N-1–C-5–C-6	110.8(9)	C-4–C-5–C-6	111.5(9)
O-6–C-6–C-5	109.1(9)	O-1–C-7–O-2	104.2(9)
O-1–C-7–C-8	108.8(10)	O-2–C-7–C-8	109.5(9)
O-1–C-7–C-9	111.5(10)	O-2–C-7–C-9	110.8(10)
C-8–C-7–C-9	111.7(11)	Si–C-10–C-11	113.5(9)
Si–C-10–C-12	109.8(9)	C-11–C-10–C-12	109.5(12)
Si–C-10–C-13	109.2(9)	C-11–C-10–C-13	109.7(11)
C-12–C-10–C-13	104.7(11)	O-3–C-30–O-30	119.2(10)
O-3–C-30–C-31	118.8(10)	O-30–C-30–C-31	121.7(10)
C-30–C-31–C-32	119.1(10)	C-30–C-31–C-36	122.5(11)
C-32–C-31–C-36	118.3(11)	C-31–C-32–C-33	120.8(11)
C-32–C-33–C-34	117.2(13)	C-33–C-34–C-35	122.4(14)
C-34–C-35–C-36	121.7(14)	C-31–C-36–C-35	119.6(13)
Si–C-41–C-42	120.4(10)	Si–C-41–C-46	126.7(10)
C-42–C-41–C-46	112.9(12)	C-41–C-42–C-43	121.7(14)
C-42–C-43–C-44	122.8(16)	C-43–C-44–C-45	117.0(16)
C-44–C-45–C-46	122.5(16)	C-41–C-46–C-45	122.8(13)
Si–C-51–C-52	125.1(10)	Si–C-51–C-56	119.2(9)
C-52–C-51–C-56	115.6(12)	C-51–C-52–C-53	122.0(13)
C-52–C-53–C-54	119.7(14)	C-53–C-54–C-55	120.2(17)
C-54–C-55–C-56	119.9(15)	C-51–C-56–C-55	122.4(13)

conformation (Q = 23 pm, φ = 132°). The angle between the two fused rings, defined by the torsion angle O-2–C-2–C-1–O-4, is +98°.

The C–O bond lengths in the acetal sequence C-4–O-4–C-1–O-1–C-7 show the characteristic variations observed in the methyl pyranosides and predicted from theoretical calculations[11], although the C-4–O-4–C-1–O-1 and O-4–C-1–O-1–C-7 torsion angles of +108° and −93° are different from those close to 60 or 180° observed in the acetal moiety of the pyranosides. The azido group is nearly linear. The bond angle N-1–N-2–N-3 of 170.8° agrees well with values reported for 5-azido-5-deoxy-*N*,*N*-diethyl-1,2-*O*-isopropylidene-3-*O*-methanesulphonyl-β-L-idofuranuronamide[9] and alkyl azides[12], but the C-4–C-5–N-1–N-2 torsion angle is −161.6°.

TABLE III

Torsion angle (°) for **6**

C-1–C-2...C-3–C-4	30.9	C-3–C-4...C-5–N-1	51.5
C-2–C-3...C-4–O-4	−35.0	C-3–O-3...C-30–C-31	−176.6
C-3–C-4...O-4–C-1	26.1	C-3–O-3...C-30–O-30	9.4
C-4–O-4...C-1–C-2	−6.4	C-4–C-5...C-6–O-6	176.2
O-4–C-1...C-2–C-3	−15.7	C-4–C-5...N-1–N-2	−161.6
		C-5–C-6...O-6–Si	−178.6
O-1–C-1...C-2–O-2	−25.1	C-6–C-5...N-1–N-2	75.2
O-2–C-2...C-3–O-3	44.0	C-6–O-6...Si–C-10	177.0
O-3–C-3...C-4–C-5	81.5	C-6–O-6...Si–C-41	55.5
O-1–C-1...C-2–C-3	−138.9	C-6–O-6...Si–C-51	−67.2
O-2–C-2...C-3–C-4	−78.5	C-7–O-2...C-2–C-1	18.8
O-3–C-3...C-2–C-1	153.4	O-3–C-30...C-31–C-36	−159.8
C-5–C-4...C-3–C-2	−154.3	O-4–C-4...C-5–N-1	−65.2
		O-6–Si...C-10–C-11	64.6
C-1–O-1...C-7–O-2	−11.9	O-6–Si...C-10–C-12	−58.5
C-1–O-1...C-7–C-8	−128.6	O-6–Si...C-10–C-13	−172.7
C-1–O-1...C-7–C-9	107.7	O-6–C-6...C-5–N-1	−62.0
C-2–C-3...O-3–C-30	73.8	O-30–C-30...C-31–C-32	−163.6
C-2–O-2...C-7–O-1	−5.8	O-30–C-31...C-32–C-33	177.8
C-3–C-4...C-5–C-6	174.2		

EXPERIMENTAL

For general experimental details, see ref. 13.

*3-O-Benzoyl-6-O-*tert*-butyldiphenylsilyl-1,2-O-isopropylidene-α-D-allofuranose* (**1**). — A solution of 3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-allofuranose[14] (3.0 g) in pyridine (60 mL) was stirred with 4-dimethylaminopyridine (0.1 mg) and *tert*-butyldiphenylsilyl chloride (4.73 mL, 2 equiv.) at room temperature for ~3.5 h. T.l.c. (toluene–ethyl acetate, 1:1) then showed only one fast-moving compound. The mixture was poured into ice–water and extracted with ethyl acetate, the extract was dried (Na_2SO_4), and the solvent was evaporated. Short-column chromatography (hexane–ethyl acetate, 2:1) of the residue gave syrupy **1** (4.88 g, 93.8%), $[\alpha]_D$ +74° (*c* 1, chloroform) (Found: C, 68.3; H, 6.8. $C_{32}H_{38}O_7Si$ calc.: C, 68.3; H, 6.8%). N.m.r. data ($CDCl_3$): ^1H, δ 7.1–8.1 (m, 15 H, 3 Ph), 5.86 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 5.14 (dd, 1 H, $J_{2,3}$ 5.1, $J_{3,4}$ 8.3 Hz, H-3), 4.96 (dd, 1 H, H-2), 4.45 (dd, 1 H, $J_{4,5}$ 3.9 Hz, H-4), 4.0–4.1 (m, 1 H, H-5), 3.7–3.8 (m, 2 H, H-6a,6b) 2.58 (d, 1 H, HO-5), 1.31 and 1.52 (2 s, 6 H, CMe_2), 1.06 (s, 9 H, CMe_3); ^{13}C, δ 113.0 (s, *C*Me_2), 104.4 (s, C-1), 78.0 (s, C-2 or C-4), 77.7 (s, C-4 or C-2), 72.65 (s, C-3) 71.5 (s, C-5), 64.4 (s, C-6), 26.9 [s, C(*C*$H_3)_3$], 26.65 [s, C(*C*$H_3)_2$], 19.2 (s, *C*$(CH_3)_3$].

*3-O-Benzoyl-6-O-*tert*-butyldiphenylsilyl-1,2-O-isopropylidene-5-O-methanesulphonyl-α-D-allofuranose* (**2**). — A cooled (0°) solution of **1** (19.9 g) in pyridine (67 mL) was treated with methanesulphonyl chloride (3.38 mL, 2 equiv.) for ~2 h. The mixture was worked-up in the usual manner. Short-column chromatography (ethyl acetate–hexane, 5:1) of the product gave **2** (16.2 g, 92.9%), $[\alpha]_D$ +82° (*c* 1, chloroform) (Found:

C, 61.9; H, 6.4; S, 5.0. $C_{33}H_{40}O_9SSi$ calc.: C, 61.85; H, 6.3; S, 5.0%). N.m.r. data ($CDCl_3$): ^1H, δ 7.6–8.1 (m, 15 H, 3 Ph), 5.85 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.9–5.1 (m, 3 H, H-2,3,5), 4.68 (dd, 1 H, $J_{3,4}$ 8.0, $J_{4,5}$ 3.0 Hz, H-4), 3.91 (d, 2 H, $J_{5,6a}$ 6.4 Hz, H-6a,6b), 2.97 (s, 3 H, Ms), 1.31, 1.53 (2, s, CMe_2), 1.08 (s, 9 H, CMe_3); ^{13}C, δ 113.4 (s, $\mathit{C}Me_2$), 104.3 (s, C-1), 80.4 (s, C-2), 77.7 (s, C-3 or C-4), 76.1 (s, C-4 or C-3), 72.7 (s, C-5), 62.5 (s, C-6), 38.5 (s, CH_3SO_2), 26.8 [s, $C(\mathit{C}H_3)_3$ and $C(\mathit{C}H_3)_2$], 19.2 [s, $\mathit{C}(CH_3)_3$].

*3-O-Benzoyl-5-bromo-6-O-*tert*-butyldiphenylsilyl-5-deoxy-1,2-O-isopropylidene-β-L-talofuranose* (**3**) *and -α-D-allofuranose* (**4**). — *N*,*N*-Dimethylformamide (50 mL) containing activated alumina (1.3 g) was stirred with potassium bromide (8.0 g) for 15 min. 18-Crown-6 (0.5 g) was added, followed by **2** (5.2 g). The mixture was stirred for 7 days at 90–100° under nitrogen, when t.l.c. (hexane–ethyl acetate, 9:1) showed that the reaction was complete; a major and a minor faster moving product, with similar R_F values, were formed. The mixture was poured into cold water, then extracted with dichloromethane, and the extract was washed with water, dried ($MgSO_4$), and concentrated. Flash-column chromatography (twice with hexane–ethyl acetate, 11:1) gave, first, **3** (2.1 g, 40.5%), $[\alpha]_D$ +76° (*c* 1, chloroform) (Found: C, 61.3; H, 5.9; Br, 12.35. $C_{32}H_{37}BrO_6Si$ calc.: 61.4; H, 6.0; Br, 12.8%). N.m.r. data ($CDCl_3$): ^1H, δ 7.2–8.1 (m, 15 H, 3 Ph), 5.93 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 5.12 (dd, 1 H, $J_{2,3}$ 4.9, $J_{3,4}$ 8.3 Hz, H-3), 4.97 (dd, 1 H, H-2), 4.75 (d, 1 H, $J_{4,5}$ <0.5 Hz, H-4), 3.9–4.2 (m, 3 H, H-5,6a,6b), 1.34 and 1.53 (2 s, 6 H, CMe_2), 1.10 (s, 9 H, CMe_3); ^{13}C, δ 113.3 (s, $\mathit{C}Me_2$), 104.8 (s, C-1), 77.7 (s, C-2), 75.7 (s, C-3 or C-4), 75.1 (s, C-4 or C-3), 65.0 (s, C-6), 53.2 (s, C-5), 26.8 [s, $C(\mathit{C}H_3)_3$ and $C(\mathit{C}H_3)_2$], 19.3 [s, $\mathit{C}(CH_3)_3$].

Eluted second was **4** (1.3 g, 24.9%), $[\alpha]_D$ +84° (*c* 1, chloroform) (Found: C, 61.2; H, 5.9; Br, 12.1. $C_{32}H_{37}BrO_6Si$ calc.: C, 61.4; H, 6.0; Br, 12.8%). N.m.r. data ($CDCl_3$): ^1H, δ 7.2–8.1 (m, 15 H, 3 Ph), 5.88 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.15 (dd, 1 H, $J_{2,3}$ 4.9, $J_{3,4}$ 8.1 Hz, H-3), 4.98 (dd, 1 H, H-2), 4.82 (dd, 1 H, $J_{4,5}$ 4.2 Hz, H-4), 4.27 (qd, 1 H, $J_{5,6a}$ 5.9, $J_{5,6b}$ 6.6 Hz, H-5), 3.9–4.0 (m, 2 H, H-6a,6b), 1.32 and 1.54 (2 s, 6 H, CMe_2), 1.09 (s, 9 H, CMe_3); ^{13}C, δ 113.3 (s, $\mathit{C}Me_2$), 104.55 (s, C-1), 78.3 (s, C-2 or C-4), 77.7 (s, C-4 or C-2), 75.1 (s, C-3), 65.1 (s, C-6), 53.7 (s, C-5), 26.9 [s, $C(\mathit{C}H_3)_3$ and $C(\mathit{C}H_3)_2$], 19.4 [s, $\mathit{C}(CH_3)_3$].

*5-Azido-3-O-benzoyl-6-O-*tert*-butyldiphenylsilyl-5-deoxy-1,2-O-isopropylidene-α-D-allofuranose* (**5**). — A mixture of *N*,*N*-dimethylformamide (40 mL), potassium azide (2.4 g), 18-Crown-6 (~0.1 g), and alumina (~2.0 g) was stirred with **3** (1.64 g) for 19 h at ~90°, when t.l.c. (hexane–ethyl acetate, 9:1) revealed one slightly slower moving component. Work-up in the usual way, followed by flash-column chromatography (hexane–ethyl acetate, 12:1), gave **5** (1.2 g, 77.9%), $[\alpha]_D$ + 80° (*c* 1, chloroform); ν_{max} 2110 (N_3), 1720 cm^{-1} (ester C=O) (Found: C, 64.95; H, 6.6; N, 6.4. $C_{32}H_{37}N_3O_6Si$ calc.: C, 65.4; H, 6.35; N, 7.15%). N.m.r. data ($CDCl_3$): ^1H, δ 7.2–8.2 (m, 15 H, 3 Ph), 5.85 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.9–5.1 (m, 2 H, H-2,3), 4.3–4.5 (m, 1 H, H-4), 3.7–3.9 (m, 3 H, H-5,6a,6b), 1.30 and 1.51 (2 s, 6 H, CMe_2), 1.08 (s, 9 H, CMe_3); ^{13}C, δ 113.3 (s, $\mathit{C}Me_2$), 104.45 (s, C-1), 78.0 (s, C-2), 76.55 (s, C-4), 73.6 (s, C-3), 64.3 (s, C-6), 63.8 (s, C-5), 26.9 [s, $C(\mathit{C}H_3)_3$], 26.7 [s, $C(\mathit{C}H_3)_2$], 19.2 [s, $\mathit{C}(CH_3)_3$].

*5-Azido-3-O-benzoyl-6-O-*tert*-butyldiphenylsilyl-5-deoxy-1,2-O-isopropylidene-β-L-talofuranose* (**6**). — The above reaction was repeated using **4** (0.84 g). After 5 h, t.l.c.

(hexane–ethyl acetate, 9:1) revealed one slightly faster moving compound. Work-up in the usual manner gave **6** (0.66 g, 83.6%), m.p. 114–115° (from ether–hexane), $[\alpha]_D$ +78° (*c* 1, chloroform); ν_{max} 2105 (N_3), 1720 cm^{-1} (ester C = O) (Found: C, 65.1; H, 6.3; N, 7.2. $C_{32}H_{37}N_3O_6Si$ calc.: C, 65.4; H, 6.35; N, 7.15%). N.m.r. data ($CDCl_3$): ^1H δ 7.2–8.1 (m, 15 H, 3 Ph), 5.87 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 5.09 (dd, 1 H, $J_{2,3}$ 4.9, $J_{3,4}$ 8.6 Hz, H-3), 4.93 (dd, 1 H, H-2), 4.36 (d, 1 H, $J_{4,5}$ 2.4 Hz, H-4), 3.8–4.1 (m, 2 H, H-6a,6b), 3.5–3.7 (m, 1 H, H-5), 1.30 and 1.49 (2 s, 6 H, CMe_2), 1.09 (s, 9 H, CMe_3); ^{13}C, δ 113.3 (s, $\mathit{C}Me_2$), 104.6 (s, C-1), 77.4 (s, C-2), 76.7 (s, C-4), 73.2 (s, C-3), 64.1 (s, C-6), 62.2 (s, C-5), 26.7 [s, $C(\mathit{C}H_3)_3$) and $C(\mathit{C}H_3)_2$], 19.1 [s, $\mathit{C}(CH_3)_3$].

Crystal data for **6**. — $C_{32}H_{37}N_3O_6Si$, M_r 587.7; a = 8.369(2), b = 10.813(2), c = 35.212(6) Å; orthorhombic space group $P2_12_12_1$, U = 3186.3 Å^3, Z = 4, D_x = 1.225, μ = 0.11 mm^{-1}, $F(000)$ = 1248. A single crystal of approximate size 0.4 × 0.4 × 0.4 mm was studied, using a Siemens R3m/v diffractometer, with Mo radiation (graphite monochromator). The cell parameters were determined from 34 reflections by a least-squares procedure. Intensity data were collected by an ω scan from θ = 3.0–48° (h = 0 to 9, k = 0 to 11, l = 0 to 35). Three standard reflections were measured every 97 reflections. A total of 2804 reflections were measured and 1339 with $I > 3\sigma(I)$ were used in subsequent calculations.

*Structure determination and refinement**. — The structure was determined by the direct method and refined by a full-matrix least-squares procedure, using SHELXTL PLUS on a Micro Vax 2000 computer. The carbon, nitrogen, oxygen, and silicon atoms were then refined anisotropically. The hydrogen atoms were included with isotropic temperature factors in the final R calculation, but their positions were not refined. The final refinement gave R = 0.051, wR = 0.062, max Δ/σ = 0.52 with a goodness-of-fit = 1.59; largest difference peak = 0.21 eA^{-3}. The weighting scheme used was

$$w^{-1} = \sigma^2(F) + 0.0007F^2.$$

The bond lengths and angles are given in Tables I and II.

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* Lists of final atomic parameters, anisotropic thermal parameters, and hydrogen positions are deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to BBA/DD/485/*Carbohydr. Res.*, 223 (1992) 271–278.

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