Oligosaccharide Analogues of Polysaccharides

Part 23[1])

Synthesis of a Dimeric Acetyleno Cyclodextrin from a Mannopyranose-Derived Dialkyne

by **Jürgen Stichler-Bonaparte** and **Andrea Vasella***

Laboratorium für Organische Chemie, ETH-Zürich, Universitätstrasse 16, CH-8092 Zürich

Dedicated to *Gérard Descotes*

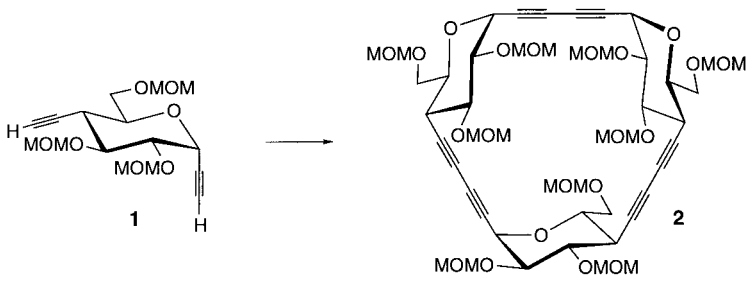
The 1,4-*cis*-diethynylated α-D-mannopyranose analogue **11** has been prepared from 1,6 :2,3-dianhydro-β-D-allopyranose (**6**) by alkynylating epoxide and acetal opening (*Scheme 2*). *Eglinton* coupling of **11** gave the cyclodimer **18** (*Scheme 3*). Crystal-structure analysis of the corresponding bis(methanesulfonate) **19** revealed substantially bent butadiyne moieties; one mannopyranosyl ring adopts the $^4C_1$ and the other one a slightly distorted $^OS_2$ conformation (*Fig. 1*). Hydrogenation of **18**, followed by deprotection, gave the stable butane-1,4-diyl-bridged cyclodimer **21** (*Scheme 3*). Crystal-structure analysis shows the $^4C_1$ conformation of the mannopyranosyl units (*Fig. 2*). The two butane fragments are characterised by a combination of *gauche* and antiperiplanar arrangements.

Introduction. – In the context of the synthesis of alkynylated saccharides, we have so far prepared up to hexadecameric cellulose analogues where the glycosidic O-atom is replaced by a butadiyne group, interrupting intramolecular, inter-residue H-bonds so as to evaluate their contribution to the supramolecular structure of cellulose (see [2] and earlier publications cited there). For this, we have synthesised glucopyranose derivatives possessing 1,4-*trans*-oriented ethynyl substituents [3][4]. We have also synthesised the isomeric α-D-glucopyranose analogues, possessing 1,4-*cis*-oriented ethynyl substituents [5]. These have been incorporated in cyclotrimeric, cyclotetrameric, and cyclohexameric analogues of cyclodextrins [6]. Remarkably, oxidative oligomerisation of the dialkyne **1** has led in a single step to the C_1-symmetric cyclotrimer **2** (*Scheme 1*), while the larger cyclooligomers were prepared by selective cross-coupling. We have also used 4-, or 1-monoethynylated glucopyranose derivatives to transform maltohexaose derivatives to maltooctaoses possessing terminal ethynyl groups, and further to cyclomaltooctaose analogues, in which a butadiyne-1,4-diyl group is replaced by one glycosidic O-atom [1].

In the course of the synthesis of these acetyleno sugars, we have devised methods for the invertive [5] or retentive [3] alkynylating opening of 1,6-anhydro-β-D-glucopyranoses, providing a rapid access to α- or β-D-glucopyranosyl-acetylenes. It was tempting to also prepare the analogous branched chain α-D-mannopyranosyl-acetylene and to examine its oxidative cyclooligomerisation. A few mannopyranosyl-acetylenes have been prepared [7–10]. Reductive dehydroxylation of an ulose

[1]) For part 22, see [1].

Scheme 1



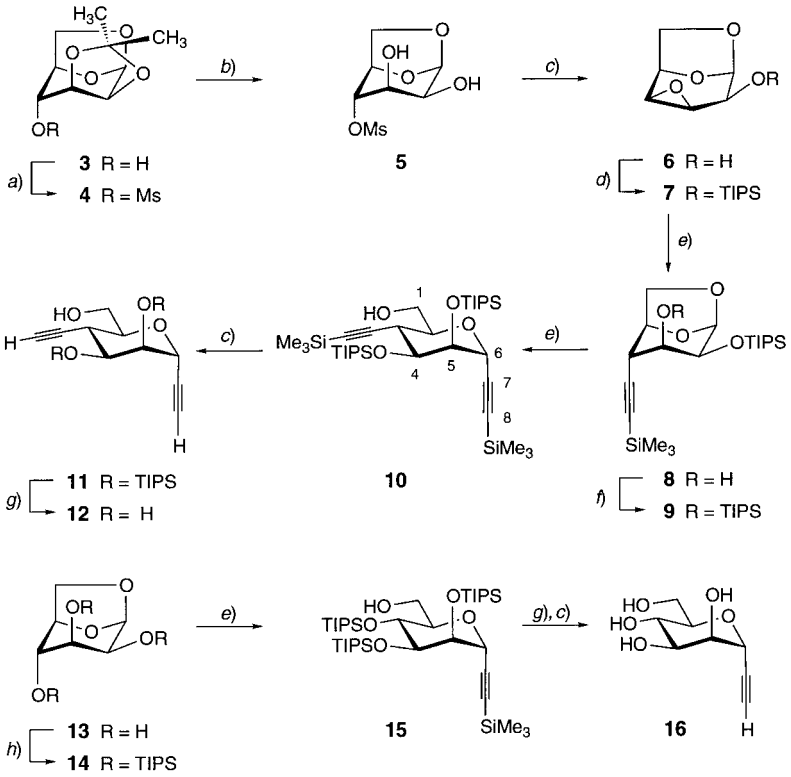
precursor led mostly to β-D-mannopyranosyl-acetylene [7]. *Isobe* and co-workers [8] have described an advantageous route to an α-D-mannopyranosyl-acetylene involving the TMSOTf-promoted reaction of an α-D-mannopyranosyl acetate with 2-(tributylstannyl)-1-(trimethylsilyl)acetylene, while 1,2-bis(trimethylsilyl)acetylene did not lead to the formation of mannopyranosyl-acetylenes. This observation, and the desire to prepare the unknown deprotected α-D-mannopyranosyl-acetylene prompted us to also examine the alkynylating ring opening of a fully *O*-substituted 1,6-anhydro-β-D-mannopyranose.

Results and Discussion. – The required branched chain α-D-mannopyranosyl-acetylenes **11** and **12** were prepared from the known 1,6:2,3-dianhydro-β-D-talopyranose (**6**) [11] (*Scheme 2*). Its preparation from the acetonide **3** [12] *via* the methanesulfonates **4** and **5** proved faster and higher yielding (82% on a 20-g scale) than the procedures involving the analogous tosylates [11][13][14]. Silylation of **6** to **7**, followed by *trans*-diaxial opening of the oxirane ring with lithium (trimethylsilyl)acetylide (LiTMSA) in the presence of $AlMe_3$ gave selectively the ethynylated 1,6-anhydromannopyranose **8**. Silylation of **8** with $(i\text{-}Pr)_3SiCl$ (TIPSCl) in pyridine failed even at elevated temperature (80°), presumably on account of the intramolecular H-bond (see below) and the shielding by the TIPSO–C(2) group, while silylation with TIPSOTf in pyridine at 80° for 24 h yielded 90% of **9**. Treatment of **9** with LiTMSA in the presence of $AlCl_3$ gave selectively the α-D-mannopyranosyl-acetylene **10** (81%). Removal of the Me_3Si groups by treatment of **10** with MeONa in MeOH provided **11**. The OTIPS groups were cleaved by treatment with aqueous TFA to yield the desired branched chain α-D-mannopyranosyl-acetylene **12** in 43% yield from **3**.

To prepare the axial ethynyl C-mannopyranoside **16**, we silylated commercial 1,6-anhydro-β-D-mannopyranose (**13**) with TIPSOTf and pyridine in $(Cl_2CH)_2$ at 110° to obtain 92% of **14** (*Scheme 2*). Treatment of **14** with 10 equiv. of LiTMSA and $AlCl_3$ led selectively to the α-D-mannopyranosyl-acetylene **15** (83%). It was deprotected by sequential treatment with aqueous TFA and NaOMe in MeOH to **16** that is thus available in three steps and an overall yield of 58% from 1,6-anhydro-β-D-mannopyranose (**13**).

The (trimethylsilyl)acetylene group of **8** is evidenced by the IR alkyne band at 2178 cm^{-1}, three new resonances in the ^{13}C-NMR spectrum at −0.04, 87.53, and 104.31 ppm, and the Me_3Si signal at 0.15 ppm in the ^1H-NMR spectrum. H–C(4) of **8** is unambiguously assigned by homodecoupling experiments, irradiation of

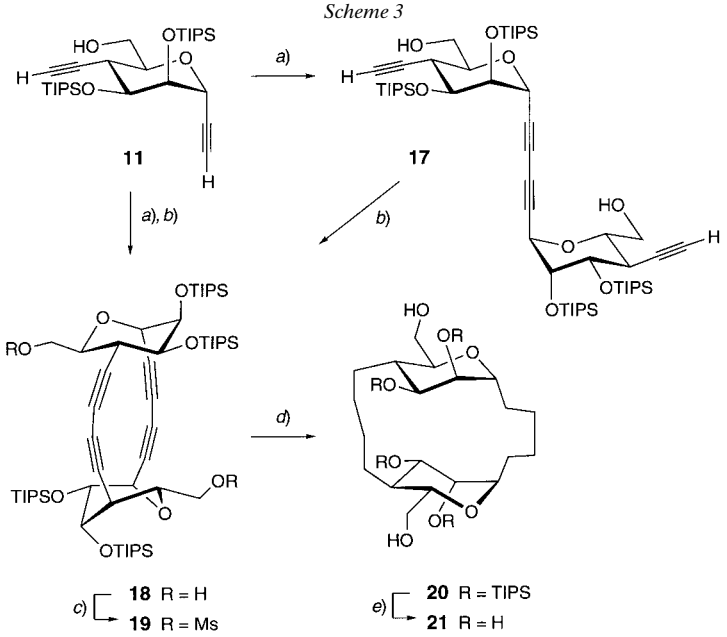
Scheme 2



a) MsCl, Et_3N, CH_2Cl_2; 88%. *b*) AcOH/H_2O 1:4; 93%. *c*) NaOMe, MeOH; 96% (**6**), 98% (**11**), 76% (**16**). *d*) TIPSOTf, pyridine/CH_2Cl_2, 23°; 99%. *e*) $Me_3SiC{\equiv}CLi$, $AlMe_3$, toluene/THF; 85% (**8**), 81% (**10**), 83% (**15**). *f*) TIPSOTf, pyridine, 80°; 90%. *g*) THF/CF_3COOH/H_2O 2:1:1; 92%. *h*) TIPSOTf, pyridine/$(Cl_2CH)_2$; 92%.

H–C(5) and H–C(3), leading to sharpening of the H–C(4) signal. This signal appears at higher field than those of H–C(2) and H–C(3) (3.00 *vs.* 3.97 and 4.11 ppm), evidencing the attachment of the ethynyl moiety at C(4). H–C(3) of **8** resonates at 4.11 ppm as a *dquint.*, showing a coupling of 4.8 Hz with the *cis*-oriented H–C(2) and couplings of *ca.* 1.6 Hz with the *trans*-oriented H–C(2), with H–C(1) and H–C(5) (*W* couplings), and with OH. These couplings evidence the *manno*-configuration and the $^1C_4$ conformation. The small J(3,OH) value reveals that HO–C(3) forms a H-bond to O–C(2) and not to O–C(6), since J(3,OH) for HO–C(3) to O–C(6) H-bonded 1,6-anhydro-β-D-glucopyranoses amounts to *ca.* 7.0 Hz [15]. The $^4C_1$ conformation of the *manno*-configured **10**–**12** is evidenced by large J(2,3) and J(3,4) values (> 10 Hz), and a small J(4,5) value (2.2–3.0 Hz). The dialkyne **10** shows an OH signal at 2.01 ppm and a br. IR band at 3499 cm^{-1}. The upfield shift of the C(1) *t* at 64.3 ppm evidences a free primary OH group and, thus, the cleavage of the acetal. The signals of the two Me_3Si moieties of **10** appear in the ^{1}H-NMR spectrum at 0.13 and 0.18 ppm, and in the ^{13}C-NMR spectrum at –0.31 and –0.25 ppm. Characteristic shifts are observed for the ethynyl C-atoms of **10**; 95.02 and 105.12 ppm are typical for an equatorial nonanomeric $Me_3SiC{\equiv}C$ group, and 89.02 and 100.00 ppm typical for an axial anomeric $Me_3SiC{\equiv}C$ group (*cf.* [5][6]). Desilylation leads to an upfield shift for the HC≡C signals of **11** and **12**; 82.7–83.0 and 72.9–73.1 ppm for the equatorial HC≡C group, and 75.5–79.4 for the axial HC≡C group. The α-D-configuration of the mannopyranosyl-acetylenes **10** and **11** is evidenced by the downfield shift of H–C(2) at 3.86–3.89 ppm and of H–C(4) at 4.41 ppm, as compared to the chemical shifts of H–C(2) and H–C(4) of related β-D-glucopyranosyl-acetylenes (3.3–3.6 ppm) [3]. In agreement with this assignment, the monoalkynes **15** and **16** show the typical ^{13}C-NMR chemical shifts for an axial anomeric acetylene group (**15**: 90.8 and 104.4 ppm; **16**: 78.7 and 79.7 ppm).

Scheme 3



a) *Ca.* 1 mM **11**, $Cu(OAc)_2$, pyridine, 23°; 77%. *b*) *Ca.* 1 mM **17**, $Cu(OAc)_2$, pyridine, 100°; 71% from **17**, 65% from **11**. *c*) MsCl, pyridine/CH_2Cl_2; 99%. *d*) H_2, Pd/C, AcOH; 79%. *f*) TBAF on silica gel, THF; 97%.

Oxidative treatment of the deprotected dialkyne **12** under similar conditions as used for the cyclotrimerisation of **1** ($Cu(OAc)_2$ in pyridine at 23° [6]) resulted in a complex mixture, while the analogous treatment of the TIPS-protected dialkyne **11** led within 2 h at 23° in a yield of 77% to the crystalline dimer **17** (*Scheme 3*). It proved inert to these reaction conditions, but reacted with $Cu(OAc)_2$ in pyridine at 100° to form the cyclodimer **18** (71%) that was also obtained by the analogous one-pot oxidation of the monomer **11** (65%). Attempts to remove the TIPS groups of **18** by treatment with $Bu_4NF \cdot 3\ H_2O$, $NEt_3 \cdot HF$, pyridine · HF, and NBS/DMSO [16–18] gave complex mixtures. The cyclodimer **18** undergoes an irreversible exothermic transition of 63 kcal/mol (DSC) in the broad temperature range of 185–250° (without formation of volatile products), and decomposed during storage at 23° within several days, while **17** showed only an endothermic transition at 118° (melting). Mesylation of **18** yielded the bis(methanesulfonate) **19** that crystallized from pentane. Pd-Catalysed hydrogenation of **18** in AcOH gave the bis(butane-1,4-diyl)-bridged dimer **20** (79%), which was deprotected with TBAF to **21**. Both the TIPS-protected cyclodimer **20** and the correponding hexol **21** are thermally stable, melting without decomposition between 218–220° and 212–213°, respectively.

The X-ray crystal structure of **19**[2]) showed bent buta-1,3-diyne moieties evidenced by $C(sp^3)-C\equiv C$ and $C\equiv C-C(sp)$ bond angles of 167 and 170.5°, respectively, for the

---

[2]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-166391 (**19**) and CCDC-166392 (**21** · MeOH). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

buta-1.3-diyne group between C(1) and C(1′), and by C(sp^3)–C≡C and C≡C–C(sp) bond angles of 159–160 and 165°, respectively, for the buta-1,3-diyne group between C(4) and C(4′) (*Fig. 1* and *Table 1*). The C≡C and C(sp)–C(sp) bond lengths (1.197 ± 0.007 and 1.383 ± 0.008 Å, resp.) show no deviation from the standard values observed in bent or linear conjugated dialkynes[3]) (for similar observations for strained

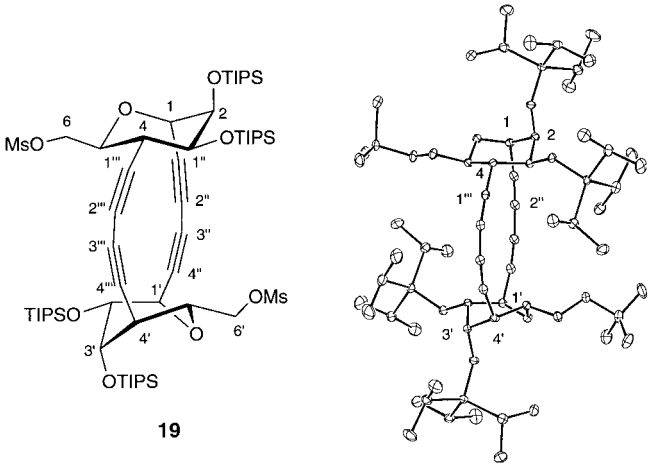


Fig. 1. *Crystal structure of the bis(buta-1,3-diyne-1,4-diyl)-bridged cyclodimer* **19**

Table 1. *Selected Bond Lengths, Atom Distances, and Bond and Dihedral Angles of the X-Ray Structure of* **19**

Bond length or atom distance [Å]				Bond or dihedral angle [°]	
C(1)–C(2)	1.544(4)	C(1)–C(1″)	1.474(4)	C(1)–C(1″)≡C(2″)	167.0(3)
C(2)–C(3)	1.524(4)	C(1″)≡C(2″)	1.195(4)	C(1″)≡C(2″)–C(3″)	170.3(4)
C(3)–C(4)	1.553(4)	C(2″)–C(3″)	1.391(4)	C(2″)–C(3″)≡C(4″)	170.5(4)
C(4)–C(5)	1.558(4)	C(3″)≡C(4″)	1.192(4)	C(3″)≡C(4″)C–(1′)	167.1(4)
C(5)–O(5)	1.418(4)	C(4″)–C(1′)	1.472(4)	C(4)–C(1‴)≡C(2‴)	160.0(3)
O(5)–C(1)	1.427(4)	C(4)–C(1‴)	1.466(4)	C(1‴)≡C(2‴)–C(3‴)	164.7(4)
C(1′)–C(2′)	1.570(5)	C(1‴)≡C(2‴)	1.203(4)	C(2‴)–C(3‴)≡C(4‴)	165.6(4)
C(2′)–C(3′)	1.525(4)	C(2‴)–C(3‴)	1.375(4)	C(3‴)≡C(4‴)–C(4′)	159.3(3)
C(3′)–C(4′)	1.556(4)	C(3‴)≡C(4‴)	1.201(4)	C(1)–C(2)–C(3)–C(4)	– 55.7
C(4′)–C(5′)	1.558(4)	C(4‴)–C(4′)	1.469(4)	C(2)–C(3)–C(4)–C(5)	48.1
C(5′)–O(5′)	1.420(4)			C(3)–C(4)–C(5)–O(5)	– 48.1
O(5′)–C(1′)	1.438(3)			C(4)–C(5)–O(5)–C(1)	57.3
				C(5)–O(5)–C(1)–C(2)	– 63.7
				O(5)–C(1)–C(2)–C(3)	62.5
C(1)···C(1′)	6.468	C(1)···C(4)	2.911	C(1′)–C(2′)–C(3′)–C(4′)	61.9
C(2)···O(5′)	7.283	C(1″)···C(1‴)	4.254	C(2′)–C(3′)–C(4′)–C(5′)	– 40.9
C(3)···C(5′)	5.650	C(2″)···C(2‴)	4.748	C(3′)–C(4′)–C(5′)–O(5′)	– 21.4
C(4)···C(4′)	6.113	C(3″)···C(3‴)	4.745	C(4′)–C(5′)–O(5′)–C(1′)	69.2
C(5)···C(3′)	6.588	C(4″)···C(4‴)	4.267	C(5′)–O(5′)–C(1′)–C(2′)	– 46.7
O(5)···C(2′)	6.594	C(1′)···C(4′)	2.962	O(5′)–C(1′)–C(2′)–C(3′)	– 18.9

[3]) Many bent cyclic butadiynes have been prepared by *Glaser*, *Hay*, and *Eglinton* coupling [19][20]. More than 15 structures possessing similar bent buta-1,3-diynyl groups are deposited with the *Cambridge Crystallographic Data Centre*; typical representatives are cyclododecadiynes or -tetraynes [21–24].

cylcoalkynes, see [19][20]). One of the tetrahydropyran rings of **19** adopts the $^4C_1$, the other a slightly distorted $^OS_2$ conformation, showing that ring strain is affecting both the linearity of the buta-1,3-diyne groups and the ring conformation. The butadiyne units of **19** lie almost in one plane and form a very small elliptical cavity, with C(1)···C(1′), C(4)···C(4′), C(2″)···C(2‴), and C(3″)···C(3‴) distances of 6.468, 6.113, 4.748, and 4.745 Å, respectively.

In the solid state, both tetrahydropyran rings of **21**·MeOH (*Fig. 2* and *Table 2*)[2]) adopt a $^4C_1$ conformation, evidencing a strongly decreased ring strain as compared with the bis(buta-1,4-diyne) **19**. As best seen in the top view (*Fig. 2,b*), the butane moiety between C(4) and C(4′) adopts an antiperiplanar arrangement for the central

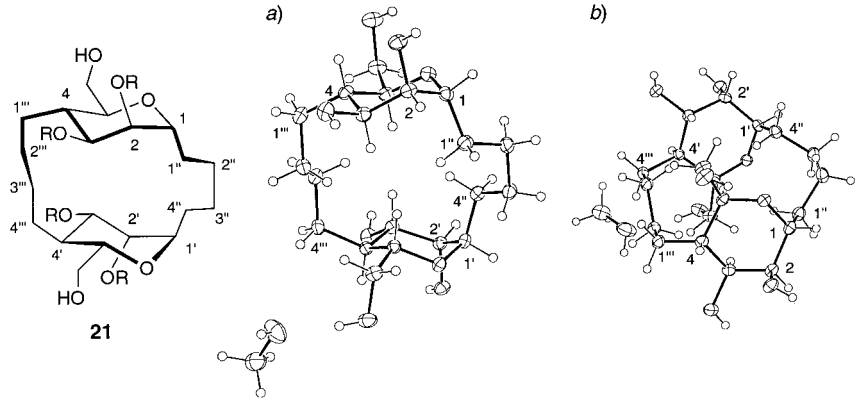


Fig. 2. *Crystal structure of the bis(butane-1,4-diyl)-bridged cyclodimer* **21**·*MeOH adduct:* a) *front view and* b) *top view*

Table 2. *Selected Bond Lengths, Atom Distances, and Dihedral Angles of the X-Ray Structure of* **21**·MeOH

Bond length or atom distance [Å]				Dihedral angle [°]	
C(1)–C(2)	1.523(3)	C(1)–C(1″)	1.522(3)	C(1)–C(2)–C(3)–C(4)	–49.1
C(2)–C(3)	1.520(3)	C(1″)–C(2″)	1.527(4)	C(2)–C(3)–C(4)–C(5)	47.6
C(3)–C(4)	1.527(3)	C(2″)–C(3″)	1.538(3)	C(3)–C(4)–C(5)–O(5)	–51.3
C(4)–C(5)	1.526(3)	C(3″)–C(4″)	1.537(3)	C(4)–C(5)–O(5)–C(1)	59.6
C(5)–O(5)	1.435(3)	C(4″)–C(1′)	1.523(3)	C(5)–O(5)–C(1)–C(2)	–59.9
O(5)–C(1)	1.437(3)	C(4)–C(1‴)	1.541(3)	O(5)–C(1)–C(2)–C(3)	53.3
C(1′)–C(2′)	1.523(3)	C(1‴)–C(2‴)	1.535(4)	C(1′)–C(2′)–C(3′)–C(4′)	–57.5
C(2′)–C(3′)	1.520(3)	C(2‴)–C(3‴)	1.530(3)	C(2′)–C(3′)–C(4′)–C(5′)	54.4
C(3′)–C(4′)	1.525(4)	C(3‴)–C(4‴)	1.533(4)	C(3′)–C(4′)–C(5′)–O(5′)	–52.6
C(4′)–C(5′)	1.535(3)	C(4‴)–C(4′)	1.544(3)	C(4′)–C(5′)–O(5′)–C(1′)	56.1
C(5′)–O(5′)	1.437(3)			C(5′)–O(5′)–C(1′)–C(2′)	–56.6
O(5′)–C(1′)	1.437(3)			O(5′)–C(1′)–C(2′)–C(3′)	56.1
C(1)···C(1′)	5.569	C(1)···C(4)	2.935	C(1)–C(1″)–C(2″)–C(3″)	–156.1
C(2)···O(5′)	6.227	C(1″)···C(1‴)	4.873	C(1″)–C(2″)–C(3″)–C(4″)	81.2
C(3)···C(5′)	4.863	C(2″)···C(2‴)	5.923	C(2″)–C(3″)–C(4″)–C(1′)	–152.7
C(4)···C(4′)	4.905	C(3″)···C(3‴)	5.803	C(4)–C(1‴)–C(2‴)–C(3‴)	–100.5
C(5)···C(3′)	5.790	C(4″)···C(4‴)	4.808	C(1‴)–C(2‴)–C(3‴)–C(4‴)	–179.9
O(5)···C(2′)	6.178	C(1′)···C(4′)	2.924	C(2‴)–C(3‴)–C(4‴)–C(4′)	–91.3

CH_2-CH_2 bond (dihedral angle of 180°) bond and a *gauche* arrangement for the peripheral CH_2-CH_2 bonds (−100 and −91°), while the butane moiety between C(1) and C(1′) adopts a *gauche* arrangement for the central CH_2-CH_2 bond (dihedral angle of 81°) and an antiperiplanar arrangement for the peripheral CH_2-CH_2 bonds (−156 and −153°). These *gauche* orientations may indicate some strain in the 16-membered ring. The planes through the mannopyranosyl units are nearly parallel (C(1)···C(1′) = 5.569 Å, C(4)···C(4′) = 6.178 Å). The OH groups of **21** are engaged in intermolecular H-bonds, HO–C(6′) as donor to MeOH.

The expected signals for the Na-adducts are observed in the ESI mass spectrum of the dimer **17** at *m*/*z* 1038 and in the MALDI-TOF mass spectrum of the cyclodimer **18** at *m*/*z* 1036. A single set of signals in the ^{1}H- and ^{13}C-NMR spectra of **17** and **18** evidences the (averaged) C_2-symmetry of these dimers. The IR absorption for HC≡C at 3315 cm^{-1}, the *Raman* transition for an isolated HC≡C bond at 2120 cm^{-1}, and the HC≡C *d* at 2.11 ppm evidence the acyclic structure of **17**. The *Raman* band of **17** at 2248 cm^{-1} indicates a buta-1,3-diyne group (typical range for dialkynylated buta-1,3-diynes: 2251–2265 cm^{-1} [25]). The formation of the bis(mannopyranosyl) butane **17** is evidenced by the H–C(1) *d* at 4.72 ppm (J = 2.2 Hz), the H–C(4) *td* (J = 10.2, 2.2 Hz). The ^{13}C-NMR signals at 82.4 and 73.1 ppm confirm the HC≡C–C(4) moiety. The buta-1,3-diyne group resonates at 72.8 and 75.3 ppm, typical for bis(hexopyranosyl)-buta-1,3-diynes [6]. The disappearance of the H–C≡C signal at 2.11 ppm and the IR band at 3315 cm^{-1} indicate an alkyne-alkyne coupling to **18**. The ring strain of **18** is evidenced by a shift towards lower wavenumbers [19][20] of the *Raman* transition (2230 cm^{-1}, compare with 2234 cm^{-1} for a similarly strained cyclododeca-1,3,7,9-tetrayne [26]) and by a downfield shift [19–21] of the *s* for the buta-1,3-diyne groups resonating at 70.6, 75.2, 78.5, and 92.8 ppm. The vicinal couplings $J(1,2)$ = 3.4, $J(2,3)$ = 3.0, $J(3,4)$ = 7.5, and $J(4,5)$ = 7.8 Hz agree with a *ca.* 1:1 contribution of the $^4C_1$ and $^OS_2$ conformer. Mesylation has no influence upon the ring strain, as **19** shows similar vicinal J(H,H) and similar δ values for the buta-1,3-diyne moiety as **18**.

The C_2 symmetry of the butanes **20** and **21** is evidenced by a single set of signals in the ^{1}H- and ^{13}C-NMR spectra. The butane fragments are revealed in ^{13}C-NMR spectrum by 4 *t* between 24.2 and 30.6 ppm. The vicinal couplings of **20** ($J(1,2)$ = 2.1, $J(2,3)$ = 2.4, and $J(3,4)$ = 10.5 Hz) evidence the $^4C_1$ conformation (signal overlapping prevented the determination of $J(4,5)$). The hexol **21**, however, shows clearly different couplings (3.4 and 5.5 Hz for $J(1,2)$ and $J(2,3)$, resp., and 6.5 Hz for $J(4,5)$), suggesting an equilibrium between $^4C_1$ and $^OS_2$ conformers. H-Bonding of HO–C(6) in CD_3OD leads to broad signals for both H–C(6) at room temperature. This broadening disappears at 55° and at −80°. The H-bonding has no influence upon the chair/boat equilibrium, since the vicinal couplings do not change. At −80°, a single set of ^{1}H-NMR signals is still observed. In the ^{13}C-NMR spectrum, broad lines are observed for the signal for C(1)/C(3) and C(5), both at 23 and 55°.

We thank the *Swiss National Science Foundation*, the *Fonds der Chemischen Industrie*, Frankfurt, and *F. Hoffmann La Roche AG*, Basel for generous support. We also thank Dr. *P. Seiler* for the crystal-structure determinations, *M. Colussi* and Prof. Dr. *R. Prins* for the DSC experiments, and Dr. *Bruno Bernet* for checking the data, critical comments, and corrections.

Experimental Part

General. See [3]. *Raman* spectra were measured on a *Perkin-Elmer* NIR-FT-spectrometer; excitation by NdYAG-*Perkin-Elmer* continous-wave laser (1064 nm). The assignment of ^{13}C-NMR *multiplets* is based on DEPT spectra; due to the characteristic J(C,H) coupling, *C*≡CH appears as a very weak positive signal, whereas C≡*C*H gives no DEPT signal. Both these signal were assigned as *s*; see also [27].

*1,6-Anhydro-2,3-*O*-isopropylidene-4-*O*-(methylsulfonyl)-β-*D*-mannopyranose* (**4**). MsCl (6.54 ml, 83 mmol) was added dropwise at −3° to a soln. of **3** [12] (12.1 g, 59 mmol) and Et_3N (13.2 ml, 94 mmol) in CH_2Cl_2 (250 ml). The mixture was stirred for 30 min at 22°, poured on ice (200 g), stirred for 2 h, and extracted with CH_2Cl_2. The combined org. layers were filtered through cotton and evaporated at 12 mbar and 20°. The slightly yellow solid (15.1 g) was dissolved in AcOEt. Filtration through silica gel (80 g, hexane/AcOEt 1:1) and crystallisation from hexane/CH_2Cl_2 2:1 gave **4** (14.5 g, 88%). White solid. R_f (toluene/AcOEt 1:1) 0.46. M.p. 130–131° (dec.). IR (KBr): 3044*m*, 3029*m*, 2983*m*, 2945*m*, 1400*w*, 1369*m*, 1330*s*, 1310*m*, 1246*m*, 1219*s*, 1174*s*, 1148*s*, 1112*m*, 1074*s*, 990*s*, 953*s*, 920*m*, 896*m*, 872*m*, 832*s*, 798*m*, 773*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.33, 1.54 (2*s*,

Me_2C); 3.15 (*s*, MsO); 3.80 (*dd*, *J* = 7.7, 6.4, H_{exo}–C(6)); 4.03 (*dd*, *J* = 7.7, 1.4, H_{endo}–C(6)); 4.11 (*dd*, *J* = 6.3, 3.0, H–C(2)); 4.31 (*dq*, *J* ≈ 6.3, 1.2, H–C(3)); 4.73 (*dq*, *J* = 6.4, 1.2, H–C(5)); 4.74 (br. *s*, H–C(4)); 5.38 (br. *d*, *J* = 3.0, H–C(1)). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 25.76, 25.83 (2*q*, *Me*$_2$C); 38.79 (*q*, MsO); 64.27 (*t*, C(6)); 71.81 (*d*, C(2)); 73.70 (*d*, C(4)); 73.86 (*d*, C(5)); 75.62 (*d*, C(3)); 99.13 (*d*, C(1)); 110.66 (*s*, Me$_2$*C*). EI-MS: 265 (44, $[M-Me]^+$), 127 (20), 100 (28), 97 (32), 85 (55), 81 (39), 69 (25), 59 (30), 43 (100). Anal. calc. for $C_{10}H_{16}O_7S$ (280.30): C 42.85, H 5.75, S 11.44; found: C 42.79, H 5.71, S 11.59.

*1,6-Anhydro-4-*O*-(methylsulfonyl)-β-*D*-mannopyranose* (**5**). A suspension of **4** (17.5 g, 62.4 mmol) in aq. AcOH/H_2O 1:4 (500 ml) was heated under reflux for 1 h. After evaporation of the resulting soln. at 12 mbar and 40°, dissolution in AcOEt, and filtration through silica gel (20 g, AcOEt) gave **5** (14.0 g, 93%). White solid. R_f (AcOEt) 0.25. M.p. 144–145° (dec.). IR (KBr): 3437*s*, 3356*s*, 3026*m*, 2978*m*, 2940*m*, 2907*m*, 1478*m*, 1440*m*, 1423*m*, 1317*s* (br.), 1265*m*, 1121*s*, 1079*s*, 1035*s*, 988*s*, 958*s* (br.), 892*s*, 861*s*, 838*s*, 807*s*, 789*m*, 730*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 3.38 (*s*, MsO); 3.44 (*dd*, *J* = 5.4, 2.0, irrad. at 5.23 → *d*, *J* = 5.4, irrad. at 3.87 → br. *d*, *J* ≈ 2.0, H–C(2)); 3.59 (*dd*, *J* = 7.4, 6.1, H_{exo}–C(6)); 3.87 (*dq*, *J* ≈ 5.2, 1.6, irrad. at 5.23 → *dt*, *J* ≈ 5.2, 1.6, H–C(3)); 4.12 (*dd*, *J* = 7.4, 1.1, H_{endo}–C(6)); 4.61 (*dq*, *J* ≈ 6.1, 1.5, irrad. at 3.87 → *dt*, *J* ≈ 6.1, 1.5, H–C(5)); 4.67 (*t*, *J* ≈ 1.8, irrad. at 3.87 → *d*, *J* ≈ 2.0, H–C(4)); 5.23 (br. *s*, irrad. at 3.87 → *d*, *J* = 2.0, H–C(1)); 4.50–5.50 (br. *s*, exchange with D_2O, HO–C(2), HO–C(3)). ^{13}C-NMR (100 MHz, (D_6)DMSO): 37.50 (*q*, MsO); 63.98 (*t*, C(6)); 65.72, 68.45 (2*d*, C(2), C(3)); 73.41 (*d*, C(4)); 79.56 (*d*, C(5)); 101.22 (*d*, C(1)). DCI-MS (MeOH): 258 (100, $[M+NH_4]^+$), 162 (95, $[M-Ms]^+$), 97 (94, $[Ms+NH_4]^+$). Anal. calc. for $C_7H_{12}O_7S$ (240.23): C 35.00, H 5.03, S 13.35; found: C 34.74, H 4.86, S 13.59.

*1,6:3,4-Dianhydro-β-*D*-taloyranose* (**6**) [20][28]. 1M NaOMe in MeOH (500 ml) was added dropwise at 23° to a suspension of **5** (98.0 g, 408 mmol) and phenolphthalein (20 mg) in MeOH (2.0 l) at a rate to maintaining a pink colour (addition of 200 ml led to a clear soln.). After the addition of further 1M NaOMe in MeOH (50 ml; TLC: complete consumption of **5**), stirring was continued for 2 h at 23°. Solid NH_4Cl was added, until the pink colour vanished. After evaporation at 12 mbar and 23°, the suspension of the residue in AcOEt, (500 ml) was washed with H_2O (80 ml, caution: the product is slightly H_2O-soluble). Evaporation at 12 mbar and 23° and crystallisation from AcOEt/pentane gave **6** (56.5 g, 96%). White solid. R_f (AcOEt) 0.40. M.p. 73–74° ([28]: 74.0–75.2°). IR and NMR, see [28].

*1,6:3,4-Dianhydro-2-*O*-(triisopropylsilyl)-β-*D*-talopyranose* (**7**). At 23°, a soln. of **6** (5.04 g, 3.5 mmol) in pyridine (75 ml) and CH_2Cl_2 (50 ml) was treated with TIPSOTf (10.9 ml, 4.2 mmol), stirred for 20 min, treated with H_2O (250 ml), stirred for 1 h, and extracted three times with CH_2Cl_2. The combined org. layers were washed with 2N H_2SO_4 and H_2O, dried ($MgSO_4$), and evaporated at 12 mbar and 40°. FC (silica gel (200 g); hexane/AcOEt 4:1) of the residue (12 g) gave **7** (10.5 g, 99%). Colourless oil. R_f (hexane/AcOEt 4:1) 0.36. R_f (toluene/AcOEt 2:3) 0.51. IR (neat): 2945*s*, 2867*s*, 1465*m*, 1148*s*, 1114*m*, 1082*s*, 980*m*, 924*m*, 882*m*, 839*m*, 813*w*, 747*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.10–1.19 (*m*, $(Me_2CH)_3Si$); 3.25 (br. *t*, *J* ≈ 3.9, irrad. at 3.96 → change, H–C(3)); 3.56 (*dd*, *J* = 6.5, 5.0, irrad. at 4.75 → *d*, *J* = 6.5, H_{exo}–C(6)); 3.68 (*t*, *J* ≈ 4.4, irrad. at 4.75 → *d*, *J* = 4.5, H–C(4)); 3.96 (*t*, *J* ≈ 3.4, irrad. at 5.26 → *d*, *J* = 3.4, H–C(2)); 4.07 (br. *d*, *J* = 6.5, H_{endo}–C(6)); 4.75 (br. *t*, *J* ≈ 4.7, H–C(5)); 5.26 (br. *d*, *J* ≈ 3.4, irrad. at 3.96 → *s*, H–C(1)). ^{13}C-NMR (50 MHz, $CDCl_3$): 12.30 (*d*, $(Me_2CH)_3$-Si); 17.95 (*q*, $(Me_2CH)_3Si$); 50.91 (*d*, C(3)); 55.95 (*d*, C(4)); 64.52 (*t*, C(6)); 68.97 (*d*, C(2)); 71.89 (*d*, C(5)); 98.87 (*d*, C(1)). DCI-MS (MeOH): 318 (11, $[M+NH_4]^+$), 301 (100, $[M+H]^+$), 257 (13), 227 (22), 211 (20). Anal. calc. for $C_{15}H_{28}O_4Si$ (300.47): C 59.96, H 9.39; found: C 59.82, H 9.37.

*1,6-Anhydro-4-deoxy-2-*O*-(triisopropylsilyl)-4-*C*-[2-(trimethylsilyl)ethynyl]-β-*D*-mannopyranose* (**8**). A cooled (ice/NaCl) soln. of (trimethylsilyl)acetylene (TMSA, 2.08 ml, 15 mmol) in toluene (20 ml) was successively treated with 1.6M BuLi in hexane (9.38 ml, 15 mmol), THF (1.0 ml), and 2.0M $AlMe_3$ in heptane (3.0 ml). The resulting colourless suspension was treated with a soln. of **5** (1.50 g, 5 mmol) in toluene (5.0 ml), heated to 65°, stirred for 75 min, cooled to 0°, treated with sat. NH_4Cl soln. (20 ml) and 2N HCl (50 ml), and extracted with AcOEt. After drying ($MgSO_4$) and evaporation at 14 mbar and 23°, FC (200 g, hexane/AcOEt 5:1 (600 ml) → 10:3 (400 ml)) of the yellow oily residue (2.3 g) gave **8** (1.69 g, 85%). Colourless oil. R_f (hexane/AcOEt 4:1) 0.40. $[\alpha]_D^{27} = -130.6$ (*c* = 1.0, MeOH). IR (neat): 3556*w*, 2956*s*, 2867*s*, 2178*m*, 1467*m*, 1250*s*, 1107*s* (br.), 1028*s*, 877*m*, 850*m*, 761*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.15 (*s*, Me_3Si); 1.05–1.14 (*m*, $(Me_2CH)_3Si$); 3.00 (br. *s*, irrad. at 4.52 → slimmer *s*, irrad. at 4.11 → slimmer *s*, H–C(4)); 3.25 (*d*, *J* = 1.7, irrad. at 4.11 → *s*, exchange with CD_3OD, HO–C(3)); 3.71 (*dd*, *J* = 7.0, 5.4, irrad. at 4.52 → *d*, *J* = 7.0, irrad. at 4.30 → *d*, *J* ≈ 5.4, H_{exo}–C(6)); 3.97 (*dd*, *J* = 4.8, 1.6, irrad. at 4.11 → *d*, *J* ≈ 1.6, H–C(2)); 4.11 (*dquint.*, *J* = 4.8, 1.6, irrad. at 4.52 → *dq*, *J* ≈ 4.8, 1.6, addn. of CD_3OD → *dq*, *J* ≈ 4.8, 1.6, H–C(3)); 4.30 (*dd*, *J* = 6.9, 0.6, irrad. at 4.52 → *d*, *J* = 6.9, H_{endo}–C(6)); 4.52 (br. *d*, *J* ≈ 4.9, irrad. at 4.11 → slimmer *d*, *J* ≈ 4.9, H–C(5)); 5.34 (br. *s*, irrad. at 4.11 → slimmer *s*, H–C(1)). ^{13}C-NMR (100 MHz, $CDCl_3$): −0.04 (*q*, Me_3Si); 12.19 (*d*, $(Me_2CH)_3Si$); 17.87 (*q*, $(Me_2CH)_3Si$); 38.87 (*d*, C(4));

67.21 (*t*, C(6)); 68.43 (*d*, C(2)); 71.65 (*d*, C(3)); 74.59 (*d*, C(5)); 87.53 (*s*, C≡*C*Si); 102.19 (*d*, C(1)); 104.31 (*s*, *C*≡CSi). DCI-MS (MeOH): 416 (14, $[M+NH_4]^+$), 400 (26), 399 (81, $[M+H]^+$), 381 (10), 357 (12), 356 (28), 355 (100, $[M-{}^i\mathrm{Pr}]^+$), 337 (9), 309 (12), 225 (9), 173 (16), 73 (19, Me_3Si^+). Anal. calc. for $C_{20}H_{38}O_4Si_2$ (398.69): C 60.25, H 9.61; found: C 60.22, H 9.53.

1,6-Anhydro-4-deoxy-2,3-bis-O-*(triisopropylsilyl)-4*-C-*[2-(trimethylsilyl)ethynyl]-β*-D-*mannopyranose* (**9**). A soln. of **8** (19.9 g, 50 mmol) in pyridine (125 ml) was treated with TIPSOTf (16.8 ml, 60 mmol), stirred at 80° for 24 h, cooled to 0°, diluted with pentane/Et_2O 5:1 (600 ml), washed with 2N HCl (4 × 50 ml) and brine (50 ml), dried ($MgSO_4$), and evaporated at 12 mbar and 23°. FC (silica gel (500 g); pentane/Et_2O 10:1) gave **9** (24.9 g, 90%). Colourless oil. R_f (hexane/Et_2O 10:1) 0.41. IR (neat): 2945*s*, 2868*s*, 2176*w*, 1466*m*, 1390*w*, 1249*m*, 1152*m*, 1111*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.15 (*s*, Me_3Si); 1.08–1.14 (*m*, 2 ($Me_2CH)_3Si$); 2.83 (*t*, $J\approx1.6$, H–C(4)); 3.72 (*dd*, $J=6.6$, 5.6, H_{exo}–C(6)); 4.01 (*dd*, $J=4.2$, 1.3, H–C(2)); 4.33 (*dq*, $J\approx4.2$, 1.5, H–C(3)); 4.40 (br. *d*, $J\approx6.8$, H_{endo}–C(6)); 4.47 (br. *d*, $J\approx5.2$, H–C(5)); 5.35 (br. *s*, H–C(1)). ^{13}C-NMR (100 MHz, $CDCl_3$): 0.00 (*q*, Me_3Si); 12.86, 13.09 (2*d*, ($Me_2CH)_3Si$); 18.10, 18.26, 18.29, 18.34 (4*q*, 2 ($Me_2CH)_3Si$); 41.59 (*d*, C(4)); 67.28 (*t*, C(6)); 70.66 (*d*, C(2)); 74.45, 74.51 (2*d*, C(3), C(5)); 88.14 (*s*, C≡*C*Si), 103.39 (*d*, C(1)); 104.67 (*s*, *C*≡CSi). DCI-MS (MeOH): 555 (25, $[M+H]^+$), 511 (42), 381 (100), 272 (35), 337 (12), 304 (14), 287 (23), 245 (12), 174 (24), 157 (19), 132 (17), 115 (13), 90 (10), 73 (21, Me_3Si^+).

2,6-Anhydro-3,7,8-trideoxy-4,5-bis-O-*(triisopropylsilyl)-8*-C-*(trimethylsilyl)-3*-C-*[2-(trimethylsilyl)ethynyl]*-D-glycero-D-manno-*oct-7-ynitol* (**10**). A soln. of TMSA (24.5 ml, 180 mmol) in toluene (150 ml) was cooled to 0–2°, treated with 2.5M BuLi in hexane (72.3 ml, 180 mmol), THF (10 ml), and $AlCl_3$ (24.0 g, 180 mmol), warmed to 23°, and stirred for 45 min. The suspension was warmed to 65°, treated with a soln. of **9** (10.0 g, 18 mmol) in toluene (30 ml), warmed to 80°, stirred for 30 min, cooled to 23°, and treated with sat. aq. NH_4Cl soln. (500 ml). After extraction with Et_2O (4 × 100 ml), the combined org. layers were dried ($MgSO_4$) and evaporated at 12 mbar and 24°. FC (silica gel (200 g); hexane/Et_2O 20:1) gave pure **10** (8.43 g, 72%) and impure fractions of **10**. FC of these fractions (silica gel (100 g); hexane/Et_2O 20:1) gave further pure **10** (1.06 g, 9%). Colourless oil. R_f (hexane/Et_2O 10:1) 0.32. IR (neat): 3603*w*, 3499*w* (br.), 2944*s*, 2893*s*, 2167*m*, 1461*s*, 1389*m*, 1333*m*, 1244*s*, 1161*s*, 1128*s* (br.), 1050*s*, 1016*s*, 883*s*, 844*s* (br.), 761*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.13, 0.18 (2*s*, 2 Me_3Si); 1.06–1.13 (*m*, 2 ($Me_2CH)_3Si$); 2.01 (br. *s*, exchange with D_2O, HO–C(1)); 3.05 (*t*, $J=10.3$, H–C(3)); 3.76 (br. *dd*, $J\approx10.4$, 5.8, addn. of $D_2O\rightarrow dd$, $J=10.4$, 5.8, H_a–C(1)); 3.86 (*ddd*, $J=10.3$, 5.6, 2.7, H–C(2)); 3.94 (br. *d*, $J\approx10.3$, addn. of $D_2O\rightarrow dd$, $J=10.3$, 2.7, H_b–C(1)); 4.07 (*t*, $J=2.3$, irrad. at 4.61 → *d*, $J=2.3$, H–C(5)); 4.41 (*dd*, $J=10.3$, 2.2, H–C(4)); 4.61 (*d*, $J=2.5$, H–C(6)). ^{13}C-NMR (100 MHz, $CDCl_3$): −0.31, −0.25 (2*q*, 2 Me_3Si); 12.88, 13.14 (2*d*, 2 ($Me_2CH)_3Si$); 18.13, 18.20, 18.40, 18.46 (4*q*, 2 ($Me_2CH)_3Si$); 34.51 (*d*, C(3)); 64.30 (*t*, C(1)); 70.60 (*d*, C(6)); 71.37 (*d*, C(4)); 73.18 (*d*, C(5)); 75.42 (*d*, C(2)); 89.02 (*s*, C(8)); 95.02 (*s*, Si*C*≡C–C(3)); 100.00 (*s*, C(7)); 105.12 (*s*, SiC≡*C*–C(3)). DCI-MS (MeOH): 655 (15, $[M+H]^+$), 654 (25, M^+), 609 (26, $[M-{}^i\mathrm{Pr}]^+$), 479 (100), 469 (17), 353 (16), 305 (49), 173 (9).

2,6-Anhydro-3,7,8-trideoxy-3-C-*ethynyl-4,5-bis*-O-*(triisopropylsilyl)*-D-glycero-D-manno-*oct-7-ynitol* (**11**). A soln. of **10** (6.00 g, 9.18 mmol) in MeOH (100 ml) was treated with NaOMe (570 mg, 10.6 mmol), stirred at reflux for 2 h, cooled to 0°, and treated with NH_4Cl (1.0 g). After evaporation at 10 mbar and 23°, the suspension of the residue in Et_2O (250 ml) was washed with H_2O (50 ml) and brine (2 × 50 ml), followed by re-extraction of the combined aq. layers with Et_2O (2 × 20 ml). The combined org. layers were dried ($MgSO_4$), and evaporated at 10 mbar and 35°. Filtration over silica gel (50 g, hexane/Et_2O 10:1) gave **11** (4.57 g, 98%). White solid. R_f (toluene/MeOH 10:1) 0.56. M.p. 80–81°. IR (KBr): 3463*m*, 3309*s*, 3256*s*, 2944*s*, 2866*s*, 2112*w*, 1465*s*, 1386*m*, 1366*m*, 1244*m*, 1168*s*, 1128*s*, 1104*m*, 1071*m*, 1052*m*, 1032*m*, 1016*m*, 996*m*, 965*m*, 920*w*, 883*s*, 849*s*, 795*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.07–1.12 (*m*, 2 ($Me_2CH)_3Si$); 1.93 (*t*, $J=6.6$, exchange with D_2O, HO–C(1)); 2.09 (*d*, $J=2.4$, irrad. at. 3.05 → *s*, HC≡C–C(3)); 2.62 (*d*, $J=2.3$, irrad. at 4.65 → *s*, H–C(8)); 3.05 (*td*, $J\approx10.3$, 2.3, H–C(3)); 3.79 (*dt*, $J\approx11.6$, 5.9, addn. of $D_2O\rightarrow dd$, $J=11.6$, 5.9, H_a–C(1)); 3.89 (*ddd*, $J=10.3$, 5.8, 2.5, irrad. at 3.05 → *dd*, $J\approx5.8$, 2.8, H–C(2)); 3.95 (*ddd*, $J=11.6$, 6.6, 2.5, addn. of $D_2O\rightarrow dd$, $J=11.6$, 2.5, H_b–C(1)); 4.10 (*t*, $J=2.3$, irrad. at 4.65 → *d*, $J=2.2$, H–C(5)); 4.41 (*dd*, $J=10.3$, 2.2, irrad. at 3.05 → *d*, $J=2.2$, H–C(4)); 4.65 (*t*, $J=2.3$, H–C(6)). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 12.95, 13.20 (2*d*, 2 ($Me_2CH)_3Si$); 18.13, 18.19, 18.41, 18.43 (4*q*, 2 ($Me_2CH)_3Si$); 33.16 (*d*, C(3)); 63.99 (*t*, C(1)); 70.03 (*d*, C(6)); 71.36 (*d*, C(4)); 72.87 (*s*, HC≡C–C(3)); 73.02 (*d*, C(5)); 75.55 (*d*, C(2)); 77.74 (*s*, C(8)); 78.62 (*s*, C(7)); 82.67 (*s*, HC≡*C*–C(3)). DCI-MS (MeOH): 510 (19), 509 (47, $[M+1]^+$), 465 (89, $[M-{}^i\mathrm{Pr}]^+$), 411 (32), 397 (17), 335 (18), 291 (93), 267 (33), 261 (41), 249 (31), 173 (100), 161 (52), 157 (88), 131 (89), 115 (77). Anal. calc. for $C_{28}H_{52}O_4Si_2$ (508.89): C 66.09, H 10.30; found: C 66.32, H 10.26.

2,6-Anhydro-3,7,8-trideoxy-3-C-*ethynyl*-D-glycero-D-manno-*oct-7-ynitol* (**12**). A soln. of **11** (800 mg, 1.6 mmol) in THF/H_2O/CF_3COOH 2:1:1 (48 ml) was stirred for 25 h at 80°. After evaporation at 12 mbar and 40°, the soln. of the residue in H_2O (100 ml) was washed with pentane (3 × 20 ml) and evaporated at

12 mbar and 40°. Two FC (silica gel (100 g); AcOEt/MeOH 10:1; 20 g, AcOEt) gave **12** (347 mg, 92%). Colourless foam. R_f (AcOEt/MeOH 10:1) 0.18. R_f (AcOEt/MeOH 5:1) 0.30. M.p. 101–102°. IR (KBr): 3400*s* (br.), 3291*s*, 2934*m*, 2116*w*, 1406*m*, 1339*m*, 1203*m*, 1136*m*, 1090*s*, 1025*m*, 989*w*, 957*m*, 841*w*, 789*w*. ^{1}H-NMR (500 MHz, CD_3OD): 2.50 (*d*, $J=2.4$, irrad. at 2.73 → *s*, HC≡C−C(3)); 2.73 (*td*, $J=10.7$, 2.3, irrad. at 3.97 → *dd*, $J\approx10.5$, 2.0, H−C(3)); 3.12 (*d*, $J=2.4$, irrad. at 4.70 → *s*, H−C(8)); 3.74 (*dd*, $J=11.9$, 5.5, H_a−C(1)); 3.81 (*td*, $J=2.6$, 0.4, irrad. at 4.70 → br. *d*, $J=2.5$, H−C(5)); 3.85 (*ddd*, $J=10.7$, 5.5, 2.2, irrad. at 2.73 → *dd*, $J=5.5$, 2.2, H−C(2)); 3.87 (*dd*, $J=11.9$, 2.2, H_b−C(1)); 3.97 (*dd*, $J=10.7$, 3.0, irrad. at 2.73 → *d*, $J=3.0$, H−C(4)); 4.70 (*t*, $J\approx2.3$, H−C(6)). ^{13}C-NMR (125 MHz, CD_3OD, assignment based on a HSQC.GRASP spectrum): 33.90 (*d*, C(3)); 64.95 (*t*, C(1)); 70.69 (*d*, C(6)); 70.81 (*d*, C(4)); 71.61 (*d*, C(5)); 73.11 (*s*, HC≡C−C(3)); 76.49 (*d*, C(2)); 79.07 (*s*, C(8)); 79.38 (*s*, C(7)); 82.95 (*s*, HC≡*C*−C(3)). DCI-MS (MeOH): 214 (100, $[M+NH_4]^+$), 197 (7, $[M+H]^+$), 165 (8), 147 (15), 124 (8), 119 (6). Anal. calc. for $C_{10}H_{12}O_4$ (196.20): C 61.22, H 6.16; found: C 61.19, H 6.12.

1,6-Anhydro-2,3,4-tris-O-*(triisopropylsilyl)-β*-D-*mannopyranose* (**14**). A soln. of **13** (648 mg, 4.0 mmol) in pyridine/$(Cl_2CH)_2$ 1:1 (10.0 ml) was treated with TIPSOTf (4.43 ml, 16 mmol), stirred at 110° for 15 h, cooled to 23°, and treated with H_2O (100 ml). After extraction with Et_2O (4 × 50 ml), the combined org. layers were washed with 2N HCl (20 ml), dried ($MgSO_4$), and evaporated at 12 mbar and 70°. FC (silica gel (60 g); hexane/Et_2O 10:1) gave **14** (2.32 g, 92%). Colourless oil. R_f (hexane/Et_2O 10:1) 0.45. IR (neat): 2944*s*, 2867*s*, 1464*m*, 1384*w*, 1367*w*, 1347*w*, 1248*w*, 1192*w*, 1154*m*, 1111*s*, 1064*m*, 1014*m*, 995*m*, 937*m*, 882*s*, 824*m*, 770*w*, 746*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.08–1.11 (*m*, 3 (Me_2CH)$_3$Si); 3.65 (*t*, $J\approx6.2$, H_{exo}−C(6)); 3.93 (*dd*, $J=4.2$, 2.2, irrad. at 5.34 → *d*, $J=4.2$, irrad. at 4.14 → br. *s*, H−C(2)); 3.97 (*t*, $J\approx2.2$, irrad. at 4.14 → *d*, $J=2.0$, H−C(4)); 4.14 (*dq*, $J\approx4.1$, 1.7, irrad. at 5.34 → *dt*, $J=4.0$, 1.7, H−C(3)); 4.35 (br. *dt*, $J\approx6.0$, 2.0, irrad. at 4.14 → br. *dd*, $J\approx6.0$, 2.0, H−C(5)); 4.36 (*dd*, $J=6.5$, 0.6, H_{endo}−C(6)); 5.34 (*t*, $J\approx1.5$, irrad. at 4.14 → br. *s*, H−C(1)). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.47, 12.85, 13.10 (3*d*, 3 (Me_2*C*H)$_3$Si); 17.99, 18.07, 18.21, 18.32, 18.41 (5*q*, 3 (*Me*$_2$CH)$_3$Si); 64.66 (*t*, C(6)); 70.25, 74.38, 75.45, 76.32 (4*d*, C(2), C(3), C(4), C(5)); 103.15 (*d*, C(1)). DCI-MS (MeOH)): 648 (1, $[M+NH_4]^+$), 631 (2, $[M+1]^+$), 587 (45), 541 (10), 457 (100), 413 (29), 411 (14), 385 (29), 372 (32), 304 (10), 287 (26), 185 (12), 157 (15), 115 (10). Anal. calc. for $C_{33}H_{70}O_5Si_3$ (631.17): C 62.80, H 11.18; found: C 62.71, H 11.02.

2,6-Anhydro-3,4,5-tris-O-*(triisopropylsilyl)-8*-C-*(trimethylsilyl)*-D-glycero-D-manno-*oct-7-ynitol* (**15**). Treatment of **14** (631 mg, 1.0 mmol), similarly as described for the conversion of **9** to **10**, gave **15** (609 mg, 83%) after workup and FC (silica gel (140 g); hexane/AcOEt 10:1). Colourless oil. R_f (hexane/Et_2O 10:1) 0.35. IR (neat): 3467*w*, 2946*s*, 2871*s*, 2173*w*, 1463*m*, 1391*m*, 1367*m*, 1250*s*, 1103*s* (br.), 1068*s*, 1034*s*, 999*s*, 947*m*, 919*m*, 884*s*, 856*s*, 843*s*, 781*m*, 761*s*. ^{13}C-NMR (100 MHz, $CDCl_3$): −0.30 (*q*, Me_3Si); 13.21 (*d*, 3 (Me_2*C*H)$_3$Si); 18.07, 18.13, 18.38, 18.41 (4*q*, 3 (*Me*$_2$CH)$_3$Si); 61.85 (*t*, C(1)); 64.44 (*d*, C(3)); 68.17 (*d*, C(6)); 72.70 (*d*, C(4)); 75.69 (*d*, C(5)); 79.79 (*d*, C(2)); 90.77 (*s*, C(8)); 104.44 (*s*, C(7)). ESI-MS: 752 (22), 751 (36, $[M+Na]^+$), 747 (34), 746 (56, $[M+NH_4]^+$), 731 (35), 730 (63), 729 (100, $[M+1]^+$).

2,6-Anhydro-D-glycero-D-manno-*oct-7-ynitol* (**16**). A soln. of **15** (360 mg, 0.49 mmol) in THF/CF_3COOH/H_2O 2:1:1 (40 ml) was kept at reflux for 67 h and evaporated at 12 mbar and 50°. A soln. of the residue in H_2O (50 ml) was washed with AcOEt (3 × 5 ml) and evaporated. FC (silica gel (20 g); AcOEt/MeOH/H_2O 17:3:2) gave a white solid (96 mg), which was dissolved in 0.01M NaOMe in MeOH (20 ml) and stirred at 23° for 1.5 h. After the addition of phenolphthalein (2 mg), the pink soln. was treated portionwise with NH_4Cl until disappearance of the colour. Evaporation at 12 mbar and 23° and FC (silica gel (20 g); AcOEt/MeOH/H_2O 17:3:2) gave **14** (70 mg, 76%). White solid. R_f (AcOEt/MeOH/H_2O 17:3:2) 0.41. M.p. 73–74°. IR (neat): 3371*s* (br.), 3302*s*, 2116*w*, 1437*m*, 1335*m*, 1205*s*, 1143*s*, 1091*s*, 1026*s*, 959*w*, 916*w*, 842*w*, 802*m*. ^{1}H-NMR (500 MHz, CD_3OD): 3.09 (*d*, $J=2.4$, irrad. at 4.65 → *s*, H−C(8)); 3.60 (*t*, $J=9.4$, H−C(3)); 3.69–3.74 (*m*, H_a−C(1), H−C(2)); 3.81–3.85 (*m*, H_b−C(1)); 3.85 (*dd*, $J=9.4$, 3.3, H−C(4)); 3.91 (*dd*, $J=3.3$, 2.1, irrad. at 4.65 → *d*, $J=3.3$, H−C(5)); 4.65 (*t*, $J=2.2$, H−C(6)). ^{13}C-NMR (125 MHz, CD_3OD, assignment based on a HSQC.GRASP spectrum): 62.86 (*t*, C(1)); 68.60 (*d*, C(3)); 70.49 (*d*, C(6)); 72.88 (*d*, C(4)); 73.94 (*d*, C(5)); 77.42 (*d*, C(2)); 78.70 (*s*, C(8)); 79.67 (*s*, C(7)). HR-ESI-MS (positive mode): 206.1031 ($C_8H_{16}NO_5$, $[M+NH_4]^+$; calc. 206.1028).

*1,1′-(Buta-1,3-diyne-1,4-diyl)bis[(1*R*)-1,5-anhydro-4-deoxy-4*-C-*ethynyl-2,3-bis*-O-*(triisopropylsilyl)*-D-*mannitol]* (**17**). A soln. of **11** (200 mg, 0.39 mmol) in pyridine (5 ml) was treated with $Cu(OAc)_2$ (713 mg, 3.9 mmol), stirred at 23° for 6 d, concentrated to 1 ml at 10 mbar and 23°, and diluted with H_2O (30 ml). After extraction with Et_2O (4 × 30 ml), the combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated at 10 mbar and 23°. FC (silica gel (20 g); hexane/AcOEt 5:1) followed by FC (silica gel (100 g); pentane/toluene/AcOEt 5:5:1) gave **17** (153 mg, 77%). White solid. R_f (toluene/MeOH 10:1) 0.45. M.p. 116–118°. IR (KBr): 3472*m*, 3315*m*, 2944*s*, 2892*s*, 2867*s*, 1465*m*, 1386*w*, 1367*w*, 1249*w*, 1162*s*, 1129*s*, 887*m*, 884*m*,

857*m*, 799*w*. *Raman* (neat): 2943*m*, 2890*m*, 2865*m*, 2248*s*, 2120*w*, 1470*w*, 1241*w*, 883*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.08–1.13 (*m*, 2 (Me_2CH)$_3$Si); 1.8–2.1 (br. *s*, HO–C(6)); 2.11 (*d*, J = 2.4, HC≡C–C(4)); 3.07 (br. *td*, $J \approx$ 10.2, 2.2, H–C(4)); 3.80 (*dd*, J = 11.3, 5.5, H_a–C(6)); 3.87 (*ddd*, J = 10.3, 5.5, 2.2, H–C(5)); 3.98 (*dd*, $J \approx$ 11.3, 1.9, H_b–C(6)); 4.11 (br. *t*, $J \approx$ 2.2, H–C(2)); 4.33 (*dd*, J = 10.3, 2.1, H–C(3)); 4.72 (*d*, J = 2.2, H–C(1)). ^{13}C-NMR (125 MHz, $CDCl_3$, assignment based on a HSQC.GRASP spectrum): 12.87, 13.45 (2*d*, 2 (Me_2CH)$_3$Si); 18.07, 18.13, 18.37, 18.40 (4*q*, 2 (Me_2CH)$_3$Si); 33.04 (*d*, C(4)); 63.85 (*t*, C(6)); 70.52 (*d*, C(1)); 71.68 (*d*, C(3)); 72.82 (*s*, *C*≡C–C(1)); 73.08 (*s*, H*C*≡C–C(4)); 73.01 (*d*, C(2)); 75.29 (*s*, C≡*C*–C(1)); 76.09 (*d*, C(5)); 82.37 (*s*, HC≡*C*–C(4)). ESI-MS (MeOH/AcOH): 1039 (85), 1038 (100, $[M + Na]^+$), 1016 (44, $[M + H]^+$).

*1,1′:4,4′-Bis(buta-1,3-diyne-1,4-diyl)bis[(1*R*)-1,5-anhydro-4-deoxy-2,3-bis*-O-*(triisopropylsilyl)*-D-*mannitol]* (**18**). a) *From* **17**: A soln. of **17** (1.02 g, 1.0 mmol) in pyridine (1.0 l) was treated with $Cu(OAc)_2$ (564 mg, 3.0 mmol), stirred at 100° for 7 h, and evaporated at 30 mbar and 40°. A suspension of the residue in pentane (250 ml) was washed with 2N HCl (2 × 20 ml), 25% aq. NH_3 soln. (20 ml), and brine (3 × 20 ml), dried ($MgSO_4$), and evaporated at 12 mbar and 23°. Filtration through a pad of silica gel (5 × 1 cm, pentane) and FC (pentane/AcOEt 20:3) gave **18** (722 mg, 71%).

b) *From* **11**: A soln. of **11** (509 mg, 1 mmol) in pyridine (50 ml) was treated with $Cu(OAc)_2$ (377 mg, 2 mmol), stirred at 23° for 3 d, and transferred *via* a cannula into a soln. of $Cu(OAc)_2$ (377 mg, 2 mmol) in pyridine (500 ml). The mixture was stirred at 100° for 7 h and concentrated to 5 ml at 40° and 30 mbar. The suspension of the residue in pentane (250 ml) was washed with 2N HCl (3 × 20 ml), 25% aq. NH_3 soln. (20 ml), and brine (2 × 20 ml), dried ($MgSO_4$), and evaporated. FC (silica gel (100 g); pentane/AcOEt 20:3) of the residue (408 mg) gave **18** (329 mg, 65%). White solid. R_f (cyclohexane/AcOEt 10:1) 0.43. M.p. >180° (decomp.). IR (KBr): 3484*w* (br.), 3311*w*, 2945*s*, 2890*m*, 2868*s*, 1464*m*, 1390*w*, 1243*w*, 1164*s*, 1116*s*, 1099*s*, 1015*m*, 883*s*. *Raman* (neat): 2946*s*, 2890*m*, 2865*s*, 2230*s*, 1470*w*, 1240*w*, 881*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.04–1.11 (*m*, 2 (Me_2CH)$_3$Si); 2.12 (br. *s*, HO–C(6)); 2.63 (*t*, $J \approx$ 7.7, H–C(4)); 3.67 (*dd*, J = 11.7, 4.8, H_a–C(6)); 3.81 (*dd*, J = 11.6, 2.7, H_b–C(6)); 4.16 (*ddd*, J = 7.8, 4.2, 2.7, H–C(5)); 4.22 (*t*, $J \approx$ 3.2, H–C(2)); 4.54 (*dd*, J = 7.5, 3.0, H–C(3)); 4.58 (*d*, J = 3.4, H–C(1)). ^{13}C-NMR (125 MHz, $CDCl_3$): 12.89, 13.21 (2*d*, 2 (Me_2CH)$_3$Si); 18.13, 18.19, 18.34, 18.38 (4*q*, 2 (Me_2CH)$_3$Si); 36.38 (*d*, C(4)); 64.15 (*t*, C(6)); 70.64 (*s*, *C*≡C); 70.70 (*d*, C(1)); 72.61 (*d*, C(3)); 74.05 (*d*, C(2)); 75.18 (*s*, *C*≡C); 77.34 (*d*, C(5)); 78.47 (*s*, *C*≡C); 92.81 (br. *s*, *C*≡C). MALDI-TOF-MS: 1036 ($[M + Na]^+$). Anal. calc. for $C_{56}H_{100}O_8Si_4$ (1013.74): C 66.35, H 9.94; found: C 66.35, H 9.77.

*1,1′:4,4′-Bis(buta-1,3-diyne-1,4-diyl)bis[(1*R*)-1,5-anhydro-4-deoxy-6-*O*-(methylsulfonyl)-2,3-bis*-O-*(triisopropylsilyl)*-D-*mannitol]* (**19**). A soln. of **18** (101 mg, 0.10 mmol), pyridine (200 µl, 2.48 mmol), and MsCl (80 µl, 1 mmol) in CH_2Cl_2 (5.0 ml) was stirred at 23° for 16 h, treated with H_2O (5 ml), and stirred for 2 h. After extraction with CH_2Cl_2 (2 × 20 ml), the combined org. layers were washed with brine, filtered through cotton, and evaporated. FC (silica gel (10 g); heptane/AcOEt 10:3) gave **19** (108 mg, 99%). White solid, decomposing at 23° within several days. R_f (heptane/AcOEt 10:3) 0.24. IR (KBr): 2944*s*, 2866*s*, 1732*w*, 1464*s*, 1352*s*, 1243*m*, 1185*s*, 1134*s*, 1090*s*, 1009*s*, 984*s*, 883*s*, 848*s*, 796*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.09–1.12 (*m*, 2 (Me_2CH)$_3$Si); 2.49 (*t*, $J \approx$ 7.2, H–C(4)); 3.02 (*s*, MsO); 4.27 (br. *t*, $J \approx$ 3.0, H–C(2)); 4.27–4.36 (*m*, H–C(5), H_a–C(6)); 4.37 (*dd*, J = 9.7, 6.1, H_b–C(6)); 4.53 (*dd*, J = 7.1, 3.0, H–C(3)); 4.60 (*d*, J = 3.3, H–C(1)). ^{13}C-NMR (100 MHz, $CDCl_3$): 12.92, 13.13 (2*d*, 2 (Me_2CH)$_3$Si); 18.11, 18.19, 18.32, 18.27 (4*q*, 2 (Me_2CH)$_3$Si); 36.47 (*d*, C(4)); 37.63 (*q*, MsO); 69.87 (*t*, C(6)); 70.88 (*d*, C(1)); 70.91 (*s*, *C*≡C); 72.52 (*d*, C(3)); 73.79 (*d*, C(2)); 74.64 (*d*, C(5)); 75.32 (*s*, *C*≡C); 78.48 (*s*, *C*≡C); 90.96 (br. *s*, *C*≡C).

X-Ray Analysis of **19**. Crystallisation of **19** from pentane by slow evaporation of the solvent at ambient temp. for 18 h gave crystals suitable for X-ray analysis. $C_{58}H_{104}O_{12}S_2Si_4$ (1169.89); monoclinic, *P*2(1) no. 4; a = 19.782(2) Å, b = 8.406(2) Å, c = 21.157(5) Å, β = 106.42(1)°; V = 3374.7(12) Å^3; D_x = 1.151 Mg/m^3; Z = 2. Intensities were measured in the ω-scan mode on an *Enraf-Nonius CAD-4* diffractometer with CuK_α radiation (λ = 1.54180 Å) at 170 K, Θ range 2.18–59.94°. Of the 5541 total collected reflections, 5223 independent reflections were observed. R = 0.0301, R_w = 0.0804. The structure was solved with the direct-methods routine of SHELXS-86, and the refinement was performed with SHELXL-93 [29].

*1,1′:4,4′-Bis(butane-1,4-diyl)bis[(1*R*)-1,5-anhydro-4-deoxy-2,3-bis*-O-*(triisopropylsilyl)*-D-*mannitol]* (**20**). A suspension of **18** (40 mg, 0.0395 mmol) and 10% Pd on charcoal (40 mg) in AcOH (2.0 ml) was hydrogenated (6 bar of H_2) at 23° for 16 h and filtered through *Celite* (2 g, Et_2O). Evaporation and filtration through silica gel (1.5 g, cyclohexane/Et_2O 30:1) gave **20** (32 mg, 79%). White solid. R_f (cyclohexane/Et_2O 20:1) 0.43. M.p. 218–220°. IR (KBr): 3544*s*, 3478*s*, 3416*s*, 2946*s*, 2867*s*, 1466*m*, 1385*w*, 1239*w*, 1163*m*, 1136*m*, 1106*m*, 1083*m*, 1087*m*, 1029*m*, 932*w*, 883*m*, 842*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.07–1.11 (*m*, 2 (Me_2CH)$_3$Si); 1.18–1.26 (*m*, 2 H); 1.34–1.46 (*m*, 3 H); 1.50–1.65 (*m*, 2 H); 2.05–2.23 (*m*, 3 H, 1 H exchanged with D_2O); 3.61 (*dt*, $J \approx$ 10.8, 5.4, addn. of D_2O → *dd*, $J \approx$ 11.5, 6.6, H_a–C(6)); 3.74–3.79 (*m*, addn. of D_2O → change, H–C(1), H–C(5),

H_b–C(6)); 3.93 (*t*, *J* = 2.1, H–C(2)); 4.07 (*dd*, *J* = 10.5, 2.4, H–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.49, 13.52 (2*d*, 2 (Me_2CH)$_3$Si); 18.33, 18.38, 18.40, 18.52 (4*q*, 2 (Me_2CH)$_3$Si); 24.21, 24.25, 27.17, 28.25 (4*t*, 2 CH_2CH_2); 38.29 (*d*, C(4)); 64.10 (*t*, C(6)); 68.04 (*d*, C(1)); 71.38 (*d*, C(3)); 74.24 (*d*, C(2)); 78.31 (*d*, C(5)). MALDI-TOF-MS: 1051 ([*M* + Na]$^+$). Anal. calc. for $C_{56}H_{116}O_8Si_4$ (1029.87): C 65.31, H 11.35; found: C 65.36, H 11.10.

*1,1′:4,4′-Bis(butane-1,4-diyl)bis[(1*R*)-1,5-anhydro-4-deoxy-*D*-mannitol]* (**21**). A soln. of **20** (50 mg, 485 μmol) in THF (5 ml) was treated with TBAF on silica gel (440 mg, 1.1 mmol F^-/g, 0.485 mmol), stirred at 23° for 15 h and at 40° for 3 h, treated with MeOH (5.0 ml), and stirred for 20 min. After filtration and washing the solid with MeOH (30 ml), evaporation of the combined filtrate, and washings at 12 mbar and 30° gave a yellow oil (250 mg). FC (silica gel (6 g); AcOEt/MeOH/H_2O 15 : 3 : 1) followed by FC (silica gel (5 g); CH_2Cl_2/MeOH 10 : 3) gave **21** (19 mg, 97%). White solid. R_f (AcOEt/MeOH/H_2O 15 : 3 : 2) 0.23. R_f (CH_2Cl_2/MeOH 10 : 3) 0.16. IR (KBr): 3419*s* (br.), 2948*s*, 2867*m*, 1638*m*, 1616*m*, 1461*w*, 1411*w*, 1383*w*, 1344*w*, 1261*w*, 1185*w*, 1129*m*, 1068*m*, 979*w*, 918*w*, 868*w*, 801*w*, 734*m*. ^{1}H-NMR (300 MHz, CD_3OD, 55°): 1.20–1.40 (*m*, 3 H), 1.40–1.90 (*m*, 6 H) (2 CH_2CH_2, H–C(4)); 3.63 (*dd*, *J* = 11.7, 2.8, H_a–C(6)); 3.645 (*dd*, *J* = 5.5, 3.4, H–C(2)); 3.75 (*td*, *J* = 6.5, 2.8, H–C(5)); 3.79–3.86 (*m*, H–C(1), H–C(3)); 3.92 (*dd*, *J* = 11.7, 6.7, H_b–C(6)). ^{1}H-NMR (400 MHz, CD_3OD, 23°): 1.20–1.40 (*m*, 3 H), 1.40–1.90 (*m*, 6 H) (2 CH_2CH_2, H–C(4)); 3.61 (br. *d*, *J* ≈ 12.0, H_a–C(6)); 3.645 (*dd*, *J* = 5.5, 3.4, H–C(2)); 3.75 (*td*, *J* = 6.5, 2.8, H–C(5)); 3.80–3.85 (*m*, H–C(1), H–C(3)); 3.90–4.05 (br. *s*, H_b–C(6)). ^{1}H-NMR (400 MHz, CD_3OD, −80°): 1.18–1.38 (*m*, 5 H), 1.38–2.05 (*m*, 4 H) (2 CH_2CH_2, H–C(4)); 3.21 (br. *d*, *J* ≈ 12.0, H_a–C(6)); 3.30 (br. *s*, H–C(2)); 3.48–3.90 (*m*, H–C(1), H–C(3), H–C(5)), H_b–C(6)). ^{13}C-NMR (75 MHz, CD_3OD, 23°): 24.93, 26.96, 27.24, 30.46 (4*t*, 2 CH_2CH_2); 40.60 (br. *d*, C(4)); 64.13 (*t*, C(6)); 69.57 (br. *d*, C(1), C(3)); 74.03 (*d*, C(2)); 74.5 (br. *d*, C(5)). ^{13}C-NMR (75 MHz, CD_3OD, 55°): 25.01, 27.04, 27.38, 30.55 (4*t*, 2 CH_2CH_2); 40.71 (*d*, C(4)); 64.44 (*t*, C(6)); 69.91 (br. *d*, C(1), C(3)); 74.18 (*d*, C(2)); 74.96 (br. *d*, C(5)). ESI-MS: 427 (51, [*M* + Na]$^+$), 242 (100).

X-Ray Analysis of **21** · *MeOH*. Crystallisation of **21** from MeOH by slow evaporation of the solvent at ambient temp. gave crystals of **21** · MeOH suitable for X-ray analysis. M.p. 212–213°. $C_{20}H_{36}O_8 \cdot CH_4O$ (436.53); orthorhombic, *P*2(1)2(1)2(1); *a* = 8.472(2), *b* = 14.498(3), *c* = 18.271(6) Å; *V* = 2244.2(10) Å^3; D_x = 1.292 Mg/m^3; *Z* = 4. Intensities were measured in the ω-scan mode on an *Enraf-Nonius CAD-4* diffractometer with CuK_α radiation (λ = 1.54180 Å) at 223 K, Θ range 3.89–64.88°. Of the 2230 total collected reflections, 2184 independent reflections were observed. *R* = 0.0304, R_w = 0.0787. The structure was solved by direct methods (SIR92 [30]), and refined by full-matrix least-squares analysis (SHELXL97 [29]), using an isotropic extinction correction (heavy atoms anisotropic, H-atoms isotropic). Most H-positions of CH groups are based on stereochemical considerations, those of OH groups were located from an electron-density difference-map and refined without restraints.

REFERENCES

[1] B. Hoffmann, D. Zanini, I. Ripoche, R. Bürli, A. Vasella, *Helv. Chim. Acta* **2001**, *84*, 1862.
[2] T. V. Bohner, O.-S. Becker, A. Vasella, *Helv. Chim. Acta* **1999**, *82*, 198.
[3] J. Alzeer, C. Cai, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 242.
[4] J. Alzeer, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 177.
[5] R. Bürli, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 1159.
[6] R. Bürli, A. Vasella, *Helv. Chim. Acta* **1997**, *80*, 2215.
[7] T. Lowary, M. Meldal, A. Helmboldt, A. Vasella, K. Bock, *J. Org. Chem.* **1998**, *63*, 9657.
[8] T. Nishikawa, M. Ishikawa, M. Isobe, *Synlett* **1999**, 123.
[9] A. Dondoni, G. Mariotti, A. Marra, *Tetrahedron Lett.* **2000**, *41*, 3483.
[10] T. M. Davis, T. L. Lowary, *Carbohydr. Res.* **2000**, *324*, 210.
[11] R. M. Hann, C. S. Hudson, *J. Am. Chem. Soc.* **1942**, *64*, 925.
[12] M. A. Zottola, R. Alonso, G. D. Vite, B. Fraser-Reid, *J. Org. Chem.* **1989**, *54*, 6123.
[13] J. Stanek, M. Cerny, *Synthesis* **1972**, 698.
[14] S. Ogawa, Y. Nakamura, *Carbohydr. Res.* **1992**, *226*, 79.
[15] C. Li, B. Bernet, A. Vasella, E. A. Broger, A. Meili, *Carbohydr. Res.* **1991**, *216*, 149.
[16] T. D. Nelson, R. D. Crouch, *Synthesis* **1996**, 1031.
[17] C. Rücker, *Chem. Rev.* **1995**, *95*, 1009.
[18] R. J. Batten, A. J. Dixon, R. J. K. Taylor, *Synthesis* **1980**, 234.
[19] R. Gleiter, R. Merger, in 'Modern Acetylene Chemistry', Eds. F. Diederich and P. J. Stang, VCH, Weinheim, 1995, p. 285.

[20] M. Meier, *Adv. Strain Org. Chem*. **1991**, *1*, 215.
[21] S. K. Collins, G. P. A. Yap, A. G. Fallis, *Angew. Chem.*, *Int. Ed*. **2000**, *39*, 385.
[22] K. N. Houk, L. T. Scott, N. G. Rondan, D. C. Spellmeyer, G. Reinhardt, J. L. Hyun, G. J. Decicco, R. Weiss, M. H. M. Chen, L. S. Bass, J. Clardy, F. S. Jørgensen, T. A. Eaton, V. Sarkozi, C. M. Petit, L. Ng, K. D. Jordan, *J. Am. Chem. Soc*. **1985**, *107*, 6556.
[23] R. Gleiter, R. Merger, J. Chavez, T. Oeser, H. Irngartinger, H. Pritzkow, B. Nuber, *Eur. J. Org. Chem*. **1999**, 2841.
[24] U. H. F. Bunz, V. Enkelmann, *Chem.–Eur. J.* **1999**, *5*, 263.
[25] A. G. Meister, R. F. Cleveland, *J. Chem. Phys.* **1944**, *12*, 313; I. Moggio, M. Alloisio, A. Cravino, D. Comoretto, P. Piaggio, G. F. Musso, G. Garbarino, C. Cuniberti, C. Dell'Erba, G. Dellepiane, *J. Chem. Soc.*, *Perkin Trans. 2* **1998**, 2249.
[26] L. T. Scott, G. J. DeCicco, J. L. Hyun, G. Reinhardt, *J. Am. Chem. Soc*. **1985**, *107*, 6546.
[27] T. D. W. Claridge, '*High-Resolution NMR Techniques in Organic Chemistry*', in 'Tetrahedron Organic Chemistry Series', Eds. J. E. Baldwin, F. R. S. Williams, and M. Williams, Pergamon, Amsterdam, 1999, Vol. 19, p. 142.
[28] K. Matsumoto, T. Ebata, K. Koseki, K. Okano, H. Kawakami, H. Matsuhita, *Carbohydr. Res.* **1993**, *246*, 345.
[29] G. M. Sheldrick, 'SHELXS-86, SHELXL-93, and SHELXL97: Programs for the Refinement of Crystal Structures', University of Göttingen, Germany.
[30] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr*. **1994**, *27*, 435.

Received July 6, 2001