

198. Glycosylidene Carbenes

Part 20

Synthesis of Deprotected, Spiro-Linked C-Glycosides of C₆₀

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Mannosylidenation of buckminsterfullerene (C₆₀; **1**) with the 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-protected diazirine **7** and the 2,3:4,6-di-*O*-isopropylidene-protected diazirine **8** leads to the spiro-linked C-glycosides **6** and **10** in 44 and 31% yield, respectively (*Scheme*). The diazirine **8** was prepared in five steps from 2,3:4,6-di-*O*-isopropylidene- α -D-mannopyranose (**11**) via the oximes **12**, the (*Z*)-hydroximolactone **13**, the mesylate **14**, and the diaziridines **15**. Deprotection of the mannosylidenated fullerenes **6** and **10** under acidic conditions gave the partially deprotected diol **9** (97%) and the unprotected mannosylidenated fullerene **16** (73%), respectively. The mannosylidene-fullerenes **6**, **9**, **10**, and **16** possess a 6–6 ring-bridged σ -homoaromatic structure.

Introduction. – The reaction of buckminsterfullerene (C₆₀; **1**) with glycosylidene carbenes, derived from the diazirines **2** and **3**, leads in good yields to the chiral and enantiomerically pure spiro-linked C-glycosides **4** and **5** [1]. Deprotection should give ambiphilic products with potentially interesting biological and physical properties¹). However, attempts to deprotect the glycosylidene fullerenes **4** and **5** failed under a variety of conditions. We thus required protecting groups which can be removed under reaction conditions which do not affect the C₆₀ moiety.

Protecting groups of the acetal type appeared promising, since their cleavage proceeds well under mildly acidic conditions, to which several derivatives of C₆₀ proved stable [2] [4] [6] [8] [24–26]. Glycosylidene-diazirines that are partially protected as acetals are known [27] [28].

We report here the synthesis of the mannosylidene-fullerene **6** from the known 4,6-*O*-benzylidene-protected *manno*-diazirine **7** [28] and C₆₀, and its partial deprotection, the synthesis of the 2,3:4,6-di-*O*-isopropylidene-protected *manno*-diazirine **8**, its reaction with C₆₀, and the deprotection of the resulting mannosylidene-fullerene **10**.

Results. – 1. *Preparation of the Diazirine 8.* The synthesis of **8** from 2,3:4,6-di-*O*-isopropylidene- α -D-mannopyranose (**11**) [29] was performed in five steps following an established procedure [28] [30]. The oximes **12** were obtained in 90% yield as a 2:3 (*E/Z*)-mixture, as evidenced by the ¹H-NMR signals of H–C(1) at 7.51 and 7.01 ppm. The oximes **12** were best oxidized by *N*-chlorosuccinimide (NCS) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [28] and gave the (*Z*)-hydroximolactone **13**

¹) A variety of ambiphilic derivatives of C₆₀ have been prepared [2–15], and their biological [7] [15–18] and physical properties, in particular their ability to form self-assembling monolayers [3] [9] [13] [19–24], have been investigated.

In the $^1\text{H-NMR}$ spectra of **6** and **10**, the H–C(2) signal is shifted to a lower field (5.04 and 5.45 ppm) as compared to the one of H–C(2) of the corresponding allyl α -D-pyranosides (3.88 and 4.15 ppm), due to the vicinity of the C_{60} moiety. The conformation of the pyranose ring is not significantly affected by the C_{60} moiety³⁾, and the $J(2,3)$, $J(3,4)$, and $J(4,5)$ values of **6** and **10** are similar to those of the corresponding diazirines and diaziridines. The pyranose ring adopts a $^4\text{C}_1$ conformation in **6**, and a flattened $^4\text{C}_1$ conformation in **10**, resulting from a distortion towards a half chair due to the fused 1,3-dioxolane ring. The IR spectra show the characteristic bands of the glycosylidene moiety and four bands of the fullerene moiety (**6**: 1427, 1184, 575, 526 cm^{-1} ; **10**: 1427, ca. 1196, 574, 525 cm^{-1}). The UV spectra of **6** resemble those of the previously described fullerene sugars (**6**: 430 (2710) and 496 nm (1730)). Similarly, **10** shows a band at 432 (2890) and at 492 nm (1930). The sharp band at ~ 430 nm appears to be characteristic for the closed 6–6 ring-bridged fullerenes [34].

The benzylidene acetal **6** was deprotected with $\text{TsOH} \cdot \text{H}_2\text{O}$ in toluene/MeOH at room temperature to give the partially deprotected 4,6-dihydroxy compound **9** in 97% yield⁴⁾. A similar deprotection of the isopropylidene acetal **10** gave the unprotected mannosylidened fullerene **16**.

The $^{13}\text{C-NMR}$ spectra of **9** and **16** show the same characteristics as the glycosylidened fullerenes described above. C(1) resonates at 73.27 (**9**) and 76.33 ppm (**16**), and the signals of the bridgehead C-atoms are observed at 79.10 and 77.64 ppm (**9**) and at 80.66 and 80.28 ppm (**16**). The $^1\text{H-NMR}$ spectra show signals of two (**9**) and four (**16**) OH groups (**9** in CDCl_3 : 2.69 (*d*, $J = 2.7$, HO–C(4)) and 2.21 (*t*, $J = 6.3$, HO–C(6)); **16** in $(\text{D}_8)\text{DMSO}/(\text{D}_8)$ toluene 5:2: 6.07 (*d*, $J = 4.7$, HO–C(2)), 5.39 (*d*, $J = 5.3$), 5.28 (*d*, $J = 5.5$), and 4.78 (*t*, $J = 5.7$, HO–C(6))). The pyranose ring of both **9** and **16** adopts the $^4\text{C}_1$ conformation. The IR spectra (KBr) of **9** and **16** show a broad OH band at 3422 (**9**) and at 3384 cm^{-1} (**16**). The UV spectra of the deprotected products **9** and **16** show only minor changes, as compared to those of **6** and **10**.

The CD spectra of all four mannosylidene-fullerenes **6**, **9**, **10**, and **16** clearly resemble each other with characteristic signals for all compounds in the range of 696–701 (min.), 661–666 (max.), 630–637 (min.), and 600–608 nm (max.). Below 600 nm, the spectra of **6** and **9** are still similar to each other but differ from those of **10** and **16**. In the case of the four mannosylidene-fullerenes, the different protecting groups do not affect the shape of the CD spectra in the range of ca. 600–800 nm, but the two glucosylidene-fullerenes **4** and **5** differ significantly from each other and from the mannosylidene-fullerenes, presumably due to the conformational differences between the pyranose rings of **4** and **5**.

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Experimental Part

General. See [36].

(*E*)- and (*Z*)-2,3:4,6-Di-*O*-isopropylidene-D-mannose Oxime (**12**). A soln. of **11** (4 g, 15.4 mmol) in EtOH (76 ml) was added to a suspension of Na (1.42 g, 62.2 mmol) and $\text{NH}_2\text{OH} \cdot \text{HCl}$ (8.33 g, 119.8 mmol) in boiling EtOH (208 ml). The solvent was evaporated after 50 min. The residue was taken up in CH_2Cl_2 (200 ml), washed with brine, dried (Na_2SO_4), and evaporated to give a ca. 2:3 mixture of (*E*)- and (*Z*)-isomers of **12** (3.83 g, 90%) which was used for the next step without further purification. FC (AcOEt/hexane 1:1) gave pure fractions of the (*E*)-isomer. R_f ($\text{CHCl}_3/\text{AcOEt}$ 1:1) 0.22. IR (CHCl_3): 3660w, 3565m, 3340s (sh), 2980s, 2920m, 2860m, 1750w, 1600w (sh), 1450m, 1380s, 1370s, 1310m, 1250s, 1190m, 1160s, 1130s, 1070s (sh), 1030s, 970m, 950m, 890s, 860m, 800m. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , (*E*)/(*Z*) ca. 2:3): 8.86 (br. s, 0.6 H, NOH); 8.61 (br. s, 0.4 H, NOH); 7.51 (*d*, $J = 7.2$, 0.4 H, H–C(1)); 7.01 (*d*, $J = 3.6$, 0.6 H, H–C(1)); 5.30 (*dd*, $J = 3.7$, 7.4, 0.6 H, H–C(2)); 4.83 (*dd*, $J = 1.2$, 7.3, 0.6 H, H–C(3)); 4.81 (*t'*, $J \approx 7.4$, 0.4 H, H–C(2)); 4.59 (*dd*, $J = 1.5$, 7.5, 0.4 H, H–C(3)); 3.94–3.87 (*m*, 2 H,

³⁾ The deformation of the chair conformation of **5** has been rationalized by postulating steric interactions between the C_{60} moiety and the pivaloyloxy group at C(2) [1].

⁴⁾ Glycosylation of **9** with *O*-(2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl) trichloroacetimidate [35] failed. The assumption that aggregation of **9** prevents the OH groups from being glycosylated is not in agreement with the molecular weight of 1143 (M_r , 1063.06) for **9**, as determined by osmometry (CHCl_3).

H-C(5), H_{ax}-C(6)); 3.68 (*dd*, *J* = 3.5, 10.3, 0.6 H, H_{eq}-C(6)); 3.63 (*dd*, *J* ≈ 3.9, 9.5, 0.4 H, H_{eq}-C(6)); 3.58 (*dd*, *J* = 1.5, 8.6, 0.4 H, H-C(4)); 3.45 (*dd*, *J* = 1.4, 10.0, 0.6 H, H-C(4)); 3.23 (*d*, *J* = 5.3, 0.6 H, OH); 3.04 (*d*, *J* = 5.4, 0.4 H, OH); 1.54 (*s*, 3 H, Me); 1.44 (*s*, 1.2 H, Me); 1.41 (*s*, 1.2 H, Me); 1.40 (*s*, 1.8 H, Me); 1.39 (*s*, 3 H, Me); 1.38 (*s*, 1.8 H, Me). ¹³C-NMR (50 MHz, CDCl₃): (*E*)-isomer: 149.94 (*d*, C(1)); 110.58 (*s*); 99.17 (*s*); 78.25 (*d*); 73.27 (*d*); 72.52 (*d*); 64.16 (*t*); 63.42 (*d*); 27.90 (*q*); 26.73 (*q*); 26.29 (*q*); 19.52 (*q*); (*Z*)-isomer: 152.09 (*d*, C(1)); 110.99 (*s*); 99.33 (*s*); 78.33 (*d*); 71.91 (*d*); 70.10 (*d*); 64.76 (*t*); 64.05 (*d*); 27.80 (*q*); 26.92 (*q*); 26.29 (*q*); 19.58 (*q*). CI-MS (NH₃): 293 (44, [M + NH₄]⁺), 276 (100, [M + 1]⁺), 274 (5), 260 (14), 258 (4).

(*Z*)-2,3:4,6-Di-O-isopropylidene-D-mannonhydroximo-1,5-lactone (**13**). A soln. of **12** (4 g, 14.5 mmol) and DBU (2.97 ml, 20.0 mmol) in CH₂Cl₂ (200 ml) at -20° was treated with NCS (2.66 g, 20.0 mmol). The mixture was stirred for 20 min at -20°, allowed to warm up to 0°, diluted with CH₂Cl₂ (200 ml), and washed with sat. aq. NaHCO₃ soln. The org. phase was dried (Na₂SO₄) and evaporated. Crystallization from AcOEt/hexane gave **13** (3.57 g, 90%). M.p. 171-173°. R_f (AcOEt/hexane 1:1) 0.45. [α]_D²⁵ = +25.0 (*c* = 0.41, CHCl₃). IR (KBr): 3485s (OH), 3000m, 2950w, 2895w, 1665m, 1560w, 1540w, 1470w, 1410w, 1390m (sh), 1380s, 1330s, 1310w, 1280m, 1270m (sh), 1245m, 1225m (sh), 1205m, 1180m, 1165m, 1110s, 1100s, 1075s, 1065s (sh), 1040w, 1025s, 980w, 950m, 930m, 870s, 860m (sh), 815w, 760w, 745w, 710w, 670w. ¹H-NMR (300 MHz, CDCl₃): 6.89 (*s*, OH); 4.88 (*d*, *J* = 7.3, H-C(2)); 4.40 (*t*', *J* ≈ 7.3, H-C(3)); 4.17 (*dd*, *J* = 5.1, 10.8, H_{eq}-C(6)); 3.92 (*t*', *J* ≈ 10.4, H_{ax}-C(6)); 3.91 (*dd*, *J* ≈ 7.3, 10.1, H-C(4)); 3.84-3.74 (*m*, H-C(5)); 1.56 (*s*, Me); 1.55 (*s*, Me); 1.46 (*s*, Me); 1.41 (*s*, Me). ¹³C-NMR (50 MHz, CDCl₃): 150.56 (*s*, C(1)); 111.99 (*s*); 99.95 (*s*); 76.44 (*d*); 72.25 (*d*); 70.63 (*d*); 67.81 (*d*); 61.59 (*t*); 28.67 (*q*); 27.26 (*q*); 25.39 (*q*); 18.81 (*q*). CI-MS (NH₃): 274 (100, [M + 1]⁺), 258 (10). Anal. calc. for C₁₂H₁₉NO₆ (273.29): C 52.74, H 7.01, N 5.13; found: C 52.79, H 6.85, N 4.97.

(*Z*)-(2,3:4,6-Di-O-isopropylidene-D-mannopyranosylidene)amino Methanesulfonate (**14**). A soln. of **13** (3.57 g, 13.1 mmol) in CH₂Cl₂ (150 ml) at 0° was treated with Et₃N (2.79 ml, 20 mmol) and MsCl (1.22 ml, 15.7 mmol). The mixture was stirred for 15 min, diluted with CH₂Cl₂ (50 ml), and washed with sat. aq. NaHCO₃ soln. The org. phase was dried (Na₂SO₄) and evaporated. Crystallization from AcOEt/hexane gave **14** (3.87 g, 87%). M.p. 130-132°. R_f (AcOEt/hexane 1:1) 0.37. [α]_D²⁵ = +31.4 (*c* = 1.49, CHCl₃). IR (KBr): 3440m (sh), 3040m, 3000s, 2940m, 2900m, 1750s, 1560w, 1540w, 1490w, 1470m, 1415w (sh), 1380s, 1370s, 1330m, 1310m, 1300w (sh), 1270s (sh), 1260s, 1200s, 1190s, 1170s, 1120s, 1100s, 1070s, 1050s, 1010m, 970s, 950m, 940m, 900s, 870s, 840s, 800s. ¹H-NMR (300 MHz, C₆D₆): 4.12 (*d*, *J* = 7.4, H-C(2)); 3.97 (*t*', *J* ≈ 7.2, H-C(3)); 3.68 (*dd*, *J* = 6.5, 10.3, H-C(4)); 3.61 (*dd*, *J* = 5.6, 11.1, H_{eq}-C(6)); 3.34 (*t*', *J* ≈ 10.0, H_{ax}-C(6)); 3.07 (*d*'r', *J* ≈ 5.7, 10.2, H-C(5)); 2.52 (*s*, MeS); 1.49 (*s*, Me); 1.27 (*s*, Me); 1.11 (*s*, Me); 0.90 (*s*, Me). ¹³C-NMR (50 MHz, CDCl₃): 158.24 (*s*, C(1)); 113.01 (*s*); 100.06 (*s*); 76.44 (*d*); 71.94 (*d*); 70.24 (*d*); 68.39 (*d*); 61.17 (*t*); 36.02 (*q*); 28.45 (*q*); 26.99 (*q*); 25.35 (*q*); 18.70 (*q*). Anal. calc. for C₁₃H₂₀NO₈S (350.36): C 44.56, H 5.75, N 3.99, S 9.15; found: C 44.61, H 5.62, N 3.76, S 8.93.

1,5-Anhydro-1-hydrazyl-2,3:4,6-di-O-isopropylidene-D-mannitol (**15**). Solid **14** (1 g, 2.85 mmol) was dissolved at 0° in a soln. of NH₃ in MeOH (20 ml) and stirred in a closed flask for 8 h at r.t. The solvent was evaporated at 0° and the residue taken up in Et₂O (20 ml), and the solids were filtered off. The filtrate was evaporated to give **15** (580 mg, 75%) which was used without further purification for the next step. R_f (AcOEt/hexane 3:2 + 0.5% Et₃N) 0.37. IR (CDCl₃): 3630m, 3400m, 3280m, 3030w (sh), 2940m, 2835w, 1700w (sh), 1452w, 1382m, 1377m, 1340w, 1320w, 1250m, 1195s, 1060s, 970w, 940w, 920w, 870m (sh), 850m. ¹H-NMR (300 MHz, CDCl₃): mixture of 2 diastereoisomers (*ca.* 10:1): 4.35 (*d*, *J* ≈ 8.0, H-C(2)); 4.33 (*t*', *J* ≈ 7.1, H-C(3)); 3.96 (*dd*, *J* = 6.0, 10.4, H-C(4)); 3.86 (*dd*, *J* = 5.6, 11.0, H_{eq}-C(6)); 3.73 (*t*', *J* ≈ 10.9, H_{ax}-C(6)); 3.55 (*d*'r', *J* ≈ 5.6, 10.2, H-C(5)); 2.55 (*d*, *J* = 9.3, 0.9 H, NH); 2.28 (*d*, *J* = 9.3, 0.1 H, NH); 2.12 (*d*, *J* = 9.3, 0.1 H, NH); 2.10 (*d*, *J* = 9.3, 0.9 H, NH); 1.48 (*s*, 2 Me); 1.38 (*s*, Me); 1.31 (*s*, Me). ¹³C-NMR (50 MHz, C₆D₆): major diastereoisomer: 110.10 (*s*); 99.44 (*s*); 81.22 (*s*); 76.41 (*d*); 75.31 (*d*); 71.86 (*d*); 66.65 (*d*); 61.88 (*t*); 28.68 (*q*); 27.08 (*q*); 25.13 (*q*); 18.19 (*q*). CI-MS (NH₃): 288 (3), 273 (100, [M + 1]⁺), 271 (4), 259 (3), 258 (14), 255 (3).

1,2-(2,3:4,6-Di-O-isopropylidene-D-mannopyranosylidene)-1,2-dihydrofullerene[60] (= 1,5-Anhydro-1,1-(1,2-dihydrofullerene[60])-1,2-diyyl)-2,3:4,6-di-O-isopropylidene-D-mannitol; **10**). a) A soln. of **15** (294 mg, 1.08 mmol) and Me₃N (2 ml, 21.3 mmol) in Et₂O (25 ml) under Ar at -70° was treated dropwise with a soln. of I₂ (192 mg, 0.76 mmol) in Et₂O (5 ml). The mixture was concentrated at -60° and the residue taken up in Et₂O (20 ml). The solids were filtered off and the filtrate (*ca.* 0.03M **8** in Et₂O) was immediately used for the next step. R_f (Et₂O) 0.80. CI-MS (NH₃): 260 (100 [M - N₂ + NH₄]⁺), 243 (58, [M - N₂ + 1]⁺), 202 (9), 102 (15), 58 (23).

b) A soln. of **1** (200 mg, 0.275 mmol) in toluene (200 ml) under Ar at r.t. was treated with a soln. of **8** (*ca.* 55 mmol) in Et₂O. The mixture was stirred for 5 h and concentrated. FC (toluene) gave **10** (83 mg, 31%) and **1** (82 mg, 41%). R_f (Et₂O/hexane 1:2) 0.46. UV (toluene): 432 (2889), 492 (1930). CD (toluene): 781 (0), 696 (-0.36), 682 (0), 666 (0.14), 653 (0), 632 (-0.13), 615 (0), 605 (0.03), 599 (0), 587 (-0.10), 562 (0), 516 (0.16), 467 (0.03), 440 (0.18). IR (KBr): 2984m, 2922m, 2840m, 1560w, 1540w, 1494m, 1427m (C₆₀), 1380s, 1256s, 1218s, 1196s, 1169s, 1072s, 1033m, 971w, 944w, 896w, 856s, 798w, 773w, 728m, 719w, 694w, 594w, 574m (C₆₀), 556m, 525s (C₆₀). ¹H-NMR (300 MHz,

CDCl_3): 5.45 (*d*, *J* = 5.4, H-C(2)); 4.68 (*dd*, *J* = 5.4, 7.8, H-C(3)); 4.36 (*dd*, *J* = 7.9, 9.5, H-C(4)); 4.18 (*dd*, *J* ≈ 6.3, 10.3, $\text{H}_{\text{eq}}-\text{C}(6)$); 4.10 (*t'*, *J* ≈ 10.3, $\text{H}_{\text{ax}}-\text{C}(6)$); 4.00 (*dt'*, *J* ≈ 6.3, 9.3, H-C(5)); 1.82 (*s*, Me); 1.69 (*s*, Me); 1.58 (*s*, Me); 1.56 (*s*, Me). ^{13}C -NMR (150 MHz, CDCl_3 ; assignment based on ^1H , ^{13}C -HMQC): 145.65 (*s*); 145.27 (*s*); 145.25 (*s*); 145.21 (*ca. 3s*); 145.17 (*s*); 145.14 (*ca. 3s*); 145.09 (*s*); 144.97 (*s*); 144.85 (*s*); 144.81 (*s*); 144.77 (*s*); 144.74 (*s*); 144.67 (*s*); 144.65 (*s*); 144.59 (*s*); 144.57 (*s*); 144.53 (*ca. 2s*); 144.46 (*ca. 3s*); 144.30 (*s*); 143.76 (*s*); 143.74 (*s*); 143.65 (*s*); 143.62 (*s*); 143.59 (*s*); 143.29 (*ca. 2s*); 143.07 (*ca. 7s*); 143.02 (*s*); 142.96 (*s*); 142.48 (*s*); 142.45 (*s*); 142.28 (*s*); 142.24 (*s*); 142.20 (*s*); 142.13 (*s*); 142.08 (*s*); 141.90 (*s*); 141.31 (*ca. 2s*); 141.08 (*s*); 138.86 (*s*); 138.47 137.32 (*s*); 136.63 (*s*); 111.26 (*s*); 100.30 (*s*); 79.63 (*s*); 78.52 (*s*); 75.80 (*d*, C(3)); 73.21 (*d*, C(4)); 72.98 (*d*, C(2)); 71.50 (*s*, C(1)); 70.39 (*d*, C(5)); 61.82 (*t*, C(6)); 29.06 (*q*); 28.49 (*q*); 26.66 (*q*); 18.92 (*q*). FAB-MS: 963 (3, $[M + 1]^+$), 720 (21), 307 (32), 154 (100). Anal. calc. for $\text{C}_{72}\text{H}_{18}\text{O}_5$ (962.94): C 89.81, H 1.88; found: C 89.52, H 2.15.

1,2-Dihydro-1,2-(D-mannopyranosylidene)fullerene[60] (= *1,5-Anhydro-1,1-(1,2-dihydrofullerene[60]-1,2-diyl)-D-mannitol 16*). A soln. of **10** (50 mg, 0.052 mmol) in toluene/MeOH 9:1 (10 ml) was treated with TsOH · H₂O (19.8 mg, 0.104 mmol) and stirred for 36 h at r.t. The mixture was evaporated. FC (toluene/MeOH 8:1) gave **16** (35 mg, 73%). *R_f* (toluene/MeOH 8:1) 0.23. UV (toluene): 433 (2940). CD (DMSO/toluene 2:3): 740 (0), 701 (−0.26), 678 (0), 665 (0.10), 650 (0), 637 (−0.08), 608 (0), 586 (−0.08), 568 (0), 481 (0.41). IR (KBr): 3384s, 2920s, 1541m, 1428m (C₆₀), 1384m, 1220s, 1168s, 1035s, 947m, 814w, 799w, 766w, 742w, 702m, 667w, 594w, 574m (C₆₀), 556m, 525s (C₆₀). ^1H -NMR (600 MHz, (D₆)DMSO/(D₈)toluene 5:2): 6.07 (*d*, *J* = 4.7, OH-C(2)); 5.39 (*d*, *J* = 5.3, OH); 5.28 (*d*, *J* = 5.5, OH); 5.03 (*dd*, *J* = 3.1, 4.6, H-C(2)); 4.78 (*t*, *J* = 5.7, OH-C(6)); 4.25–4.19 (*m*, H-C(3), H-C(4)); 4.05–4.01 (*m*, H_A-C(6)); 3.96–3.91 (*m*, H-C(5), H_B-C(6)). ^{13}C -NMR (150 MHz, (D₆)DMSO/(D₈)toluene 5:2; assignment based on ^1H , ^{13}C -HMQC): 146.30 (*s*); 145.82 (*s*); 145.77 (*s*); 145.47 (*s*); 145.29 (*ca. 2s*); 145.24 (*s*); 145.04 (*s*); 144.40 (*ca. 4s*); 144.38 (*ca. 3s*); 144.30 (*ca. 2s*); 144.26 (*s*); 144.16 (*s*); 144.13 (*s*); 144.08 (*s*); 143.94 (*s*); 143.91 (*s*); 143.65 (*s*); 143.61 (*s*); 143.50 (*ca. 2s*); 143.42 (*s*); 143.39 (*s*); 143.11 (*s*); 143.04 (*s*); 142.96 (*ca. 2s*); 142.55 (*s*); 142.50 (*s*); 142.39 (*s*); 142.35 (*ca. 2s*); 142.31 (*ca. 2s*); 142.27 (*ca. 3s*); 142.11 (*ca. 2s*); 141.53 (*ca. 4s*); 141.44 (*s*); 140.52 (*s*); 140.35 (*ca. 2s*); 140.30 (*s*); 138.07 (*s*); 137.89 (*s*); 136.44 (*s*); 136.27 (*s*); 82.52 (*d*, C(5)); 80.60 (*s*); 80.28 (*s*); 76.33 (*s*, C(1)); 73.39 (*d*, C(3) or C(4)); 67.53 (*d*, C(2)); 66.77 (*d*, C(4) or C(3)); 60.99 (*t*, C(6)). FAB-MS: 883 (11, $[M + 1]^+$), 721 (100), 720 (96).

1,2-(2,3-Di-O-benzyl-4,6-O-benzylidene-D-mannopyranosylidene)-1,2-dihydrofullerene[60] (= *1,5-Anhydro-2,3-di-O-benzyl-4,6-O-benzylidene-1,1-(1,2-dihydrofullerene[60]-1,2-diyl)-D-mannitol; 6*). A soln. of **1** (80 mg, 0.11 mmol) in toluene (80 ml) under Ar at r.t. was treated within 3 h with 10 portions (*ca.* 0.2 equiv.) of **7** (*ca.* 0.05M in CH_2Cl_2). The mixture was stirred for a further 3 h and evaporated. FC (CH_2Cl_2 /hexane 9:1) gave **6** (56 mg, 44%) and **1** (40 mg, 50%). *R_f* (CH_2Cl_2 /hexane 9:1) 0.45. UV (CHCl_3): 430 (2712), 496 (1729). CD (CHCl_3): 696 (−0.32), 687 (0), 661 (1.16), 630 (0.61), 600 (1.20), 549 (0), 526 (−0.40), 442 (0), 429 (0.54). IR (KBr): 3067w, 3027w, 2941w, 2880w, 1540w, 1494w, 1464w, 1452m, 1427m (C₆₀), 1368w, 1310w, 1274w, 1250w, 1220m, 1184w (C₆₀), 1163m, 1100s, 1063s, 1027m, 1003m, 982m, 963m, 910w, 840w, 799w, 742s, 726m, 695s, 641w, 594w, 575w (C₆₀), 560w, 552w, 526s (C₆₀), 500w. ^1H -NMR (600 MHz, C₆D₆): 7.70–7.00 (*m*, 15 arom. H); 5.47 (*s*, PhCH); 5.29 (*d*, *J* = 11.6, 1 H, PhCH₂); 5.18 (*d*, *J* = 11.7, 1 H, PhCH₂); 5.04 (*d*, *J* = 12.1, 1 H, PhCH₂); 5.04 (*d*, *J* = 3.1, H-C(2)); 4.99 (*t'*, *J* ≈ 9.5, H-C(4)); 4.74 (*d*, *J* = 12.2, 1 H, PhCH₂); 4.52 (*dd*, *J* = 3.0, 9.8, H-C(3)); 4.35–4.30 (*m*, H-C(5), H_{eq}-C(6)); 3.84 (*t'*, *J* = 11.4, H_{ax}-C(6)). ^{13}C -NMR (150 MHz, C₆D₆): 145.85 (*s*); 145.76 (*s*); 145.61 (*s*); 145.51 (*s*); 145.49 (*s*); 145.47 (*s*); 145.42 (*s*); 145.40 (*s*); 145.36 (*ca. 4s*); 145.32 (*s*); 145.18 (*s*); 145.14 (*s*); 145.09 (*s*); 144.92 (*s*); 144.88 (*ca. 2s*); 144.83 (*s*); 144.81 (*s*); 144.72 (*s*); 144.70 (*s*); 144.67 (*s*); 144.65 (*s*); 144.63 (*s*); 144.55 (*s*); 144.36 (*s*); 144.00 (*s*); 143.98 (*s*); 143.86 (*ca. 2s*); 143.52 (*s*); 143.51 (*s*); 143.34 (*s*); 143.32 (*s*); 143.30 (*ca. 3s*); 143.27 (*s*); 143.26 (*s*); 142.88 (*s*); 142.86 (*s*); 142.47 (*s*); 142.43 (*s*); 142.39 (*s*); 142.35 (*ca. 2s*); 142.29 (*s*); 141.56 (*s*); 141.47 (*s*); 141.43 (*s*); 141.41 (*s*); 138.72 (*ca. 2s*); 138.65 (*s*); 138.42 (*s*); 138.36 (*s*); 137.30 (*s*); 136.84 (*s*); 130.26–127.84 (*m*); 102.26 (*d*); 79.52 (*s*); 79.49 (*d*, C(4)); 78.88 (*s*, *d*, C(3)); 75.39 (*t*); 75.25 (*s*, C(1)); 74.66 (*d*, C(2)); 74.25 (*t*); 73.23 (*d*, C(5)); 68.47 (*t*, C(6)). Anal. calc. for $\text{C}_{87}\text{H}_{26}\text{O}_5$ (1151.17): C 90.77, H 2.30; found: C 91.05, H 2.55.

1,2-(2,3-Di-O-benzyl-D-mannopyranosylidene)-1,2-dihydrofullerene[60] (= *1,5-Anhydro-2,3-di-O-benzyl-1,1-(1,2-dihydrofullerene[60]-1,2-diyl)-D-mannitol; 9*). A soln. of **6** (20 mg, 0.017 mmol) in toluene/MeOH 9:1 (2 ml) was treated with TsOH · H₂O (3.3 mg, 0.017 mmol) and stirred for 48 h at 28°. The mixture was evaporated. FC (toluene/MeOH 9:1) of the residue gave **9** (18 mg, 97%). *R_f* (toluene/MeOH 9:1) 0.39. UV (CHCl_3): 431 (3053), 493 (1932). CD (CHCl_3): 700 (−0.25), 689 (0), 663 (1.06), 633 (0.55), 602 (1.10), 539 (0), 525 (−0.09), 475 (0), 432 (0.33). IR (KBr): 3422w, 3060w, 3026w, 2922w, 2870w, 1540w, 1494w, 1452m, 1426m (C₆₀), 1276w, 1251m, 1225m, 1209m, 1185w (C₆₀), 1169m, 1104s, 1093s, 1041s, 1026s, 996m, 914w, 810w, 797w, 742m, 699s, 668w, 602w, 588w, 574w (C₆₀), 554w, 525s (C₆₀). ^1H -NMR (300 MHz, CDCl_3): 7.62–7.18 (*m*, 10 arom. H); 5.10 (*s*, 2 H, PhCH₂); 4.91 (*d*, *J* = 11.9, 1 H, PhCH₂); 4.90 (*d*, *J* = 2.8, H-C(2)); 4.86 (*d*, *J* = 11.8, 1 H, PhCH₂); 4.66 (*dt'*, *J* ≈ 2.6, 9.2, addn. of D₂O → *t'*, *J* ≈ 9.2, H-C(4)); 4.22 (*dd*, *J* = 2.8, 9.4, H-C(3)); 4.17–4.07 (*m*, H-C(5), 2 H-C(6)); 2.69 (*d*, *J* = 2.7, exchange with D₂O, OH-C(4)); 2.21 (*t*, *J* = 6.3, exchange with D₂O, OH-C(6)). ^{13}C -NMR (150 MHz, CDCl_3);

assignment based on ^1H , ^{13}C -HMQC): 145.48 (s); 145.28 (s); 145.23 (s); 145.21 (s); 145.19 (s); 145.16 (s); 145.14 (s); 145.11 (s); 145.10 (s); 145.05 (2s); 144.94 (s); 144.90 (s); 144.85 (s); 144.71 (s); 144.66 (s); 144.62 (s); 144.60 (s); 144.57 (s); 144.50 (s); 144.49 (s); 144.42 (s); 144.40 (s); 144.39 (s); 144.32 (2s); 144.25 (2s); 143.75 (s); 143.66 (s); 143.57 (s); 143.53 (s); 143.27 (s); 143.19 (s); 143.05 (s); 143.02 (s); 143.01 (2s); 143.00 (s); 142.99 (s); 142.97 (s); 142.93 (s); 142.64 (s); 142.60 (s); 142.18 (s); 142.11 (s); 142.10 (s); 142.00 (s); 141.95 (s); 141.94 (s); 141.33 (s); 141.28 (s); 141.09 (s); 141.08 (s); 138.11 (s); 138.03 (s); 137.68 (s); 137.20 (s); 136.86 (s); 136.44 (s); 129.00–128.18 (m); 81.61 (d, C(3)); 80.60 (d, C(5)); 79.10 (s); 77.64 (s); 73.90 (t); 73.27 (s, C(1)); 73.02 (t); 71.43 (d, C(2)); 67.56 (d, C(4)); 62.92 (t, C(6)). Anal. calc. for $\text{C}_{80}\text{H}_{22}\text{O}_5$ (1063.06): C 90.39, H 2.09; found: C 90.26, H 2.36.

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