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Efficient Total Synthesis of the Natural Products 2,3,4,6-Tetra-*O*-galloyl-D-glucopyranose, 1,2,3,4,6-Penta-*O*-galloyl-β-D-glucopyranose and the Unnatural 1,2,3,4,6-Penta-*O*-galloyl-α-D-glucopyranose

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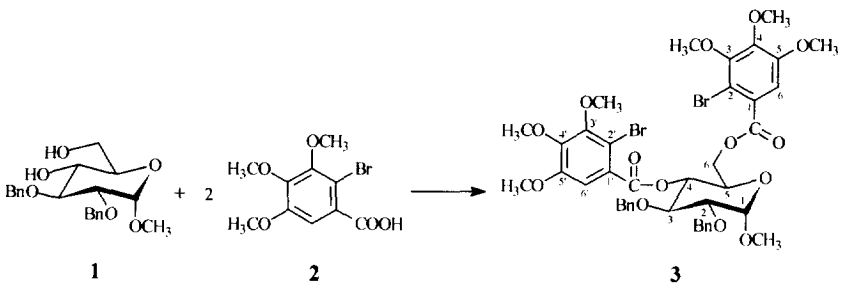
Abstract: A short synthesis of the natural products 2,3,4,6-tetra-*O*-galloyl-D-glucopyranose (**8**), 1,2,3,4,6-penta-*O*-galloyl-β-D-glucopyranose (**10**) and the unnatural 1,2,3,4,6-penta-*O*-galloyl-α-D-glucopyranose (**13**) was achieved based on a efficient esterification reaction of the benzylated gallic acid **5** with the α,β-glucopyranoses **11** and **4**, respectively. © 1997 Elsevier Science Ltd.

The natural products 1,2,3,4,6-penta-*O*-galloyl-β-D-glucopyranose (**10**) and 2,3,4,6-tetra-*O*-galloyl-D-glucopyranose (**8**) were isolated from Chinese galls by methanolysis.[1,2] These compounds possess cytotoxicity against melanoma cells (RPMI-7951) with ED_{50} values of >10 and 5.01 μg/ml, respectively.[3] Compound **10** also shows strong *in vitro* activity as inhibitor of DNA topoisomerase II[4] and both compounds inhibit protein kinase C (PKC).[5] The natural product **10** was prepared synthetically in an esterification reaction using tribenzylated gallic acid chloride and the β-D-glucopyranose employing the very long reaction time of 20 days to afford the benzylated penta-galloyl precursor that was converted to the natural compound **10** by hydrogenation.[1] The anomeric galloyl residue was cleaved by treatment of the benzylated penta-galloyl material with acetic acid-washed alumina for 16 days to afford the anomeric degalloylated compound that was subsequently converted to the natural compound **8** by hydrogenation.[1] We now report an alternative more efficient synthesis of natural products **8**, **10** and the unnatural product **13**.

Recently, Itoh[6], Lipshutz[7] and Meyers[8] published the synthesis of permethylated precursors of three natural products of the tannin class but did not describe the removal of the methyl protecting groups to the corresponding natural products. To examine the selective cleavage of the arylmethyl ethers and the methyl group at the anomeric center of the glucose core in the presence of the two ester groups, we synthesized the model compound **3** by esterification of 2-bromo-3,4,5-trimethoxybenzoic acid (**2**)[8,9] with the sugar derivative **1**[10,11] in the presence of 4-*N*,*N*-dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCC) (Scheme 1).

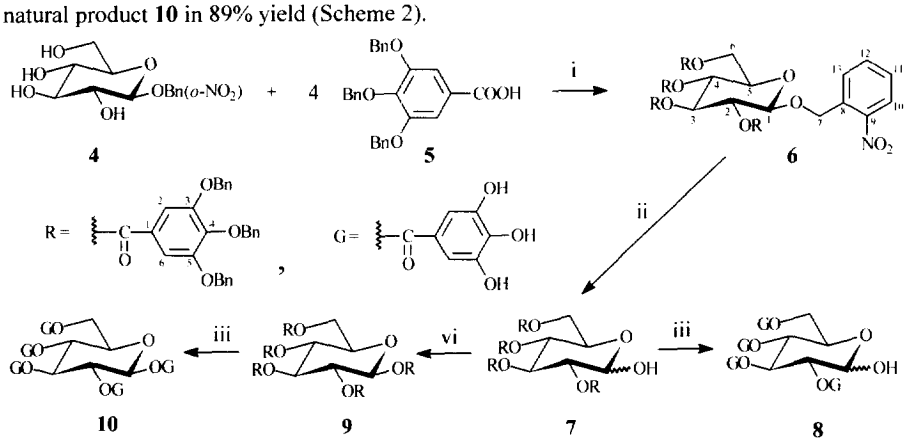


Scheme 1. Reagents and conditions: DMAP, DCC, CH_2Cl_2, reflux, 24 h

We found that the conditions required for the removal of the arylmethyl ethers by using boron tribromide in the presence of ester groups[12] under a variety of conditions (temp., time) proved in fact to be incompatible with the structural integrity of the substrate. Also, we were not able to hydrolyze the methyl group at the anomeric center of **3** under acidic conditions.[13,14]

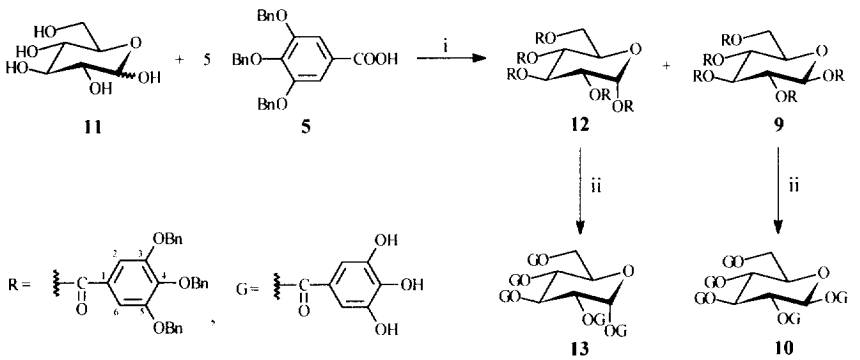
To overcome these difficulties, we decided to use benzyl ethers as the protecting groups at the aromatic systems and the photolytically cleavable *o*-nitrobenzyl protecting group at the anomeric center. The benzylated gallic acid **5**[15,16] was acylated with the anomerically protected 1-*O*-(*o*-nitrobenzyl)-β-D-glucopyranose (**4**)[17] to yield 1-*O*-(*o*-nitrobenzyl)-2,3,4,6-tetra-*O*-(3,4,5-tri-*O*-benzylgalloyl)-β-D-glucopyranose (**6**). The glycoside **6** was deprotected at the anomeric center by irradiation[18] to afford the hemiacetal **7** as an α,β-anomeric mixture. Removal of the arylbenzyl ethers of the α,β-anomeric mixture **7** was achieved by hydrogenolysis over Pd/C to furnish the natural product **8** in 90% yield as a faintly yellow powder following reversed phase thin layer chromatographic purification (Scheme 2). The lack of the C-1 galloyl group and the existence of α- and β-anomers was indicated by the appearance of two signals at δ 91.24 ppm and 96.37 ppm in the ^{13}C NMR spectrum.

For the synthesis of the natural product **10,** the anomerically deprotected compound **7** was allowed to react with the benzylated gallic acid **5**. The resultant material **9** was debenzylated using the standard protocol to give the phenolic natural product **10** in 89% yield (Scheme 2).



Scheme 2. Reagents and conditions: (i) DMAP, DCC, CH_2Cl_2, reflux, 12 h; (ii) hv; (iii) Pd/C-H_2, THF, 24 h; (vi) DMAP, DCC, benzylated gallic acid **5**, CH_2Cl_2, reflux, 36 h

In the preceding communications[19,20] we reported on the synthesis of the ellagitannins strictinin, praecoxin B and pterocarinin C using a stereoselective esterification reaction. We found a high β-selectivity in the acylation reaction of an α,β-anomeric mixture under conditions described in the literature.[21] To examine the β-selectivity under Steglich conditions,[22] the mixture of α,β-glucopyranose **11** was allowed to react with the benzylated gallic acid **5** in the presence of DMAP and DCC to afford the β-anomer **9** in 42% yield and the α-anomer **12** in 33% yield. The anomers **9** and **12** were easely separated by column chromatography on silica gel. Subsequent debenzylation of the α-anomer **12** gave the unnatural α-acylglycoside **13** and deprotection of the β-anomer **9** led to the β-configurated natural product **10**. The physical properties of the synthetic material **10** were identical to those of the natural product[23] (Scheme 3).



Scheme 3. Reagents and conditions: (i) DMAP, DCC, CH_2Cl_2, reflux, 36 h; (ii) Pd/C-H_2, THF, 24 h

EXPERIMENTAL SECTION

For general methods and instrumentation see ref..[20]

1-O-Methyl-2,3-di-O-benzyl-(2-bromo-3,4,5-tri-O-methylgalloyl)-α-D-glucopyranose (**3**): General Procedure A. A solution of sugar derivative **1** (2.00 g, 4.36 mmol), acid **2** (3.17 g, 10.90 mmol, 2.5 eq), DCC (2.34 g, 11.30 mmol, 2.6 eq) and DMAP (0.14 g, 1.13 mmol, 0.26 eq) in dry CH_2Cl_2 (70 ml) was refluxed under argon for 24 h. The reaction mixture was allowed to cool to room temperature, and the white solid (dicyclohexylurea) was filtered off. The solvent was removed *in vacuo* to give a brown oil. The oil was redissolved in CH_2Cl_2 (50 ml), washed with water (2 x 50 ml), dried (Na_2SO_4), and the solvent removed *in vacuo* to give a yellow viscous oil. Column chromatography on silica gel (CH_2Cl_2/Et_2O, 95:5) gave **3** (3.05 g, 76 %) as a white powder, m.p. 56.5–57.5 °C. $[\alpha]_D^{20}$ = +26.7° (c = 1.0, CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1} (aliphat. CH), 2850 (aliphat. CH), 1736 (CO, ester), 1581 (aromat. CC), 1483, 1452, 1387, 1340. – UV (CH_2Cl_2): λ_{max} (lg ε) = 231 nm (4.53), 259 (4.18), 300 (3.71). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.46 (s, 3 H, OCH_3), 3.66–3.71 (m, 1 H, H-2), 3.71 (s, 3 H, OCH_3), 3.90–3.95 (m, 15 H, OCH_3), 4.13 (t, $J_{3,2}$ = 9.4 Hz, $J_{3,4}$ = 9.5 Hz, 1 H, H-3), 4.15–4.25 (m, 1 H, H-5), 4.42 (dd, $J_{6,5}$ = 4.9 Hz, $J_{gem.}$ = 11.5 Hz, 1 H, H-6), 4.59–4.76 (m, 4 H, H-1, H-6, OCH_2Ph), 4.84 (d, J_{gem} = 12.1 Hz, 1 H, OCH_2Ph), 4.98 (d, J_{gem} = 11.5 Hz, 1 H, OCH_2Ph), 5.45 (t, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.7 Hz, 1 H, H-4), 7.01 (s, 1 H, Gall-H-6 or Gall-H-6'), 7.19–7.39 (m, 11 H,

H-Ar). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.15 (q, OCH_3), 56.52 (q, OCH_3), 56.67 (q, OCH_3), 61.46 (q, OCH_3), 61.58 (q, OCH_3), 64.20 (t, C-6), 67.71 (d, C-5), 71.45 (d, C-4), 73.96 and 75.75 (t, OCH_2Ph), 79.51 (d, C-3), 80.07 (d, C-2), 98.71 (d, C-1), 109.87 and 109.91 (s, Gall-C-2 and Gall-C-2'), 110.36 and 110.99 (d, Gall-C-6 and Gall-C-6'), 127.35, 127.79, 127.86, 128.55, 128.67 and 128.96 (d, C-Ar), 138.22 and 138.70 (s, Gall-C-1 and Gall-C-1'), 146.51 and 146.57 (s, Gall-C-4 and Gall-C-4'), 151.82, 151.92 and 152.78 (s, Gall-C-3, Gall-C-3', Gall-C-5 and Gall-C-5'), 165.24 and 165.92 (s, COOR). – MS (CI/NH_3, neg./300 °C): m/z (%) = 922 (10) [M^+ $^{81}Br_2$], 920 (20) [M^+ $^{79}Br^{81}Br$], 918 (12) [M^+ $^{79}Br_2$], 875 (14), 840 (8), 291 (20), 289 (20), 211 (56), 81 (99), 79 (100). – Analysis: $C_{41}H_{44}Br_2O_{14}$ (920.59) calcd. C 53.49 H 4.82; found C 53.53 H 4.90.

1-O-(o-Nitrobenzyl)-2,3,4,6-tetra-O-(3,4,5-tri-O-benzylgalloyl)-β-D-glucopyranose (**6**):
A mixture of **4** (0.28 g, 0.88 mmol), gallic acid **5** (1.70 g, 38.60 mmol, 4.4 eq), DCC (0.86 g, 42.10 mmol, 4.8 eq) and DMAP (0.43 g, 35.10 mmol, 4.0 eq) in dry CH_2Cl_2 (35 ml) was refluxed for 12 h, according to the general procedure A, to afford a viscous oil. Subsequent column chromatography on silica gel (CH_2Cl_2/*n*-hexane, 95:5) gave glucopyranose **6** (1.60 g, 91%) as a faintly green powder, m.p. 64–65.5 °C. $[\alpha]_D^{20}$ = +27.0° (c = 1.0, CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 3064 cm^{-1} (aromat. CH), 3033 (aromat. CH), 2964 (aliphat. CH), 2860 (aliphat. CH), 1724 (CO, ester), 1586 (aromat. CC), 1498 (aromat. CC), 1429, 1334, 1261. – UV ($CHCl_3$): λ_{max} (lg ε) = 273 nm (4.69). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.32–4.37 (m, 1 H, H-5), 4.49 (dd, $J_{6,5}$ = 4.5 Hz, $J_{gem.}$ = 12.0 Hz, 1 H, H-6), 4.88–4.95 (m, 1 H, H-6), 5.02–5.21 (m, 26 H, H-1, H-7, and OCH_2Ph), 5.36 (d, $J_{gem.}$ = 13.0 Hz, 1 H, H-7), 5.72–5.87 (m, 2 H, H-2 and H-4), 6.03 (t, $J_{3,2}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz, 1 H, H-3), 7.30–7.49 (m, 70 H, H-11, H-12 and H-Ar), 7.77 (d, $J_{13,12}$ = 6.4 Hz, 1 H, H-13), 8.10 (dd, $J_{10,11}$ = 7.6 Hz, $J_{10,12}$ = 1.7 Hz, 1 H, H-10). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 63.69 (t, C-6), 68.71 (t, C-7), 70.60 (d, C-4), 71.52, 71.57 and 71.68 (t, OCH_2Ph), 72.72 (d, C-2), 72.84 (d, C-5), 73.91 (d, C-3), 75.61 (t, OCH_2Ph), 101.50 (d, C-1), 109.58 and 109.73 (d, Gall-C-2 and Gall-C-6), 124.23, 124.28, 124.60 and 124.98 (s, Gall-C-1), 125.14 (d, C-10), 128.05, 128.31, 128.52, 126.61, 128.65, 128.73, 128.76, 128.86, 128.92, 128.98, 129.01 and 129.30 (d, C-11, C-13 and Ar-C), 134.09 (s, C-8), 134.34 (d, C-12), 136.80, 136.85, 136.96, 137.12, 137.83 and 137.96 (s, Ar-C), 143.12, 143.36, 143.43 and 143.56 (s, Gall-C-4), 147.29 (s, C-9), 152.96, 153.01 and 153.05 (s, Gall-C-3 and Gall-C-5), 165.41, 165.53, 166.13 and 166.27 (s, COOR). – Analysis: $C_{125}H_{105}O_{24}N$ (2005.19) calcd. C 74.87 H 5.28 N 0.70 found C 74.90 H 5.30 N 0.74.

2,3,4,6-Tetra-O-(3,4,5-tri-O-benzylgalloyl)-D-glucopyranose (**7**): A solution of **6** (0.50 g, 0.25 mmol) in tetrahydrofuran (THF) (30 ml), ethanol (30 ml) and water (5 drops) was irradiated for 7 h in a photochemical apparatus (PYREX) at 320 nm. The solvent was removed *in vacuo* to give a yellow oil. Column chromatography on silica gel (CH_2Cl_2) gave **7** (0.40 g, 86 %) as a yellow powder, m.p. 70.5–71.5 °C. $[\alpha]_D^{20}$ = +11.2° (c = 1.0, CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 3425 cm^{-1} (OH), 3063 (aromat. CH), 3035 (aromat. CH), 2921 (aliphat. CH), 2864 (aliphat. CH), 1718 (CO, ester), 1585 (aromat. CC), 1500 (aromat. CC), 1429, 1336, 1232. – UV ($CHCl_3$): λ_{max} (lg ε) = 273 nm (4.67). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.33 (dd, $J_{6,5}$ = 4.5 Hz, J_{gem} = 12.1 Hz, 1 H, H-6), 4.69–4.74 (m, 1 H, H-5), 4.79–5.17 (m, 25 H, H-6 and OCH_2Ph), 5.22 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 10.1 Hz, 1 H, H-2), 5.73 (t, $J_{4,3}$ = 10.0 Hz, $J_{4,5}$ = 9.9 Hz, 1 H, H-4), 5.82 (br. s, 1 H, H-1), 6.25 (t, $J_{3,2}$ = 10.1 Hz, $J_{3,4}$ = 10.0 Hz, 1 H, H-3), 7.20–7.47 (m, 68 H, H-Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 62.05 (t,

C-6), 66.74 (d, C-5), 68.84 (d, C-4), 69.74 (d, C-3), 70.05 and 70.18 (t, OCH_2Ph), 71.64 (d, C-2), 74.06 and 74.11 (t, OCH_2Ph), 89.43 (d, C-1), 108.03 and 108.26 (d, Gall-C-2 and Gall-C-6), 122.88, 122.91, 123.13 and 123.61 (s, Gall-C-1), 126.51, 126.54, 126.60, 126.81, 126.88, 126.93, 126.97, 127.01, 127.04, 127.08, 127.10, 127.14, 127.15, 127.22, 127.28, 127.36, 127.45 and 127.53 (d, C-Ar), 135.23, 135.27, 135.34, 135.40, 135.47, 135.60, 135.66, 136.32, 136.35 and 136.43 (s, C-Ar), 141.63, 141.78, 141.90 and 142.05 (s, Gall-C-4), 151.44 and 151.54 (s, Gall-C-3 and Gall-C-5), 164.14, 164.38, 164.74 and 164.76 (s, COOR). – Analysis: $C_{118}H_{100}O_{22}$ (1870.07) calcd. C 75.79 H 5.38 found C 75.82 H 5.45.

2,3,4,6-Tetra-O-galloyl-D-glucopyranose (**8**): General Procedure B. A suspension of **7** (0.37 g, 0.20 mmol), 10% Pd/C (0.20 g) and dry THF (10 ml) was degased with Ar (3 times) and treated with hydrogen at 40 °C for 24 h. The reaction mixture was allowed to cool to room temperature, the solid was filtered off through Celite, and the Celite was washed with acetone (30 ml). The combined organic phases were removed *in vacuo* to give a yellow oil. Reversed phase chromatography (H_2O/MeOH, 80:30) gave the α,β-anomeric mixture **8** (0.14 g, 90 %) (α/β, 72:28) as a faintly yellow powder, dec. >213 °C. To our knowledge, there are no NMR data for this α,β-anomeric mixture **8** in the literature and we now present the fully data of this compound. $[\alpha]_D^{20}$ = +45.3° (c = 0.15, acetone). – IR (KBr): $\tilde{\nu}$ = 3408 cm^{-1} (OH and aromat. CH), 2960 (aliphat. CH), 2923 (aliphat. CH), 2858 (aliphat. CH), 2364, 1701 (CO, ester), 1616 (aromat. CC), 1535 (aromat. CC), 1448, 1317. – UV (EtOAc): λ_{max} (lg ε) = 273 nm (4.41). – ^{1}H NMR (200 MHz, acetone-d_6/D_2O): δ = 4.27–4.63 (m, 6 H, H-5α, H-5β, H-6α and H-6β), 5.15 (dd, $J_{2\alpha,1\alpha}$ = 3.3 Hz, $J_{2\alpha,3\alpha}$ = 10.2 Hz, 1 H, H-2α), 5.24–5.33 (m, 2 H, H-1β and H-2β), 5.56 (d, $J_{1\alpha,2\alpha}$ = 3.3 Hz, 1 H, H-1α), 5.57 (t, J = 9.8 Hz, 2 H, H-4α and H-4β), 5.79 (t, J = 9.6 Hz, 1 H, H-3β), 6.05 (t, J = 9.9 Hz, 1 H, H-3α), 6.92–7.16 (m, 16 H, H-Arα and H-Arβ). – ^{13}C NMR (50 MHz, acetone-d_6/D_2O): δ = 63.74 (t, C-6α and C-6β), 68.67 (d, C-5α), 70.21 (d, C-4α), 70.39 (d, C-4β), 71.67 (d, C-3α), 73.18 (d, C-5β), 73.45 (d, C-2α), 74.40 (d, C-2β and C-3β), 91.24 (d, C-1α), 96.37 (d, C-1β), 110.56 and 110.60 (d, Gall-C-2 and Gall-C-6), 119.49, 119.60, 119.74, 120.03 and 120.45 (s, Gall-C-1), 138.84, 139.02, 139.12 and 139.23 (s, Gall-C-4), 145.45, 145.54 and 145.57 (s, Gall-C-3 and Gall-C-5), 165.99, 166.37, 166.77 and 166.83 (s, COOR). – MS (FAB/NBA, neg./300 °C): m/z (%) = 788 (6) [M^+], 635 (2) [M^+ - $C_7H_5O_4$], 617 (2), 459 (8), 306 (40), 199 (26), 153 (100) [$C_7H_5O_4^+$]. – Analysis: $C_{34}H_{28}O_{22}$ (788.57) calcd. C 51.79 H 3.58 found C 51.88 H 3.62.

1,2,3,4,6-Penta-O-(3,4,5-tri-O-benzylgalloyl)-α-D-glucopyranose (**12**) *and 1,2,3,4,6-Penta-O-(3,4,5-tri-O-benzylgalloyl)-β-D-glucopyranose* (**9**): Anhydrous D-(+)-glucose **11** (0.10 g, 0.56 mmol), gallic acid derivative **5** (1.83 g, 4.16 mmol, 7.5 eq), DCC (0.92 g, 4.44 mmol, 8 eq) and DMAP (0.54 g, 4.44 mmol, 8 eq) in dry CH_2Cl_2 (65 ml) were refluxed for 36 h, according to the general procedure A. Column chromatography on silica gel (CH_2Cl_2) gave **12** (0.42 g, 33 %) ($R_{f,\alpha}$ = 0.53), m.p. 71.5–72.5 °C and **9** ($R_{f,\beta}$ = 0.72) (0.53 g, 42 %), each as a white powder, m.p. 72–73 °C. **α-anomer:** $[\alpha]_D^{20}$ = +38.9° (c = 0.5, CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (aromat. CH), 3030 (aromat. CH), 2957 (aliphat. CH), 2929 (aliphat. CH), 2868 (aliphat. CH), 1728 (CO, ester), 1585 (aromat. CC), 1500 (aromat. CC), 1429, 1335, 1196. – UV (CH_2Cl_2): λ_{max} (lg ε) = 205 nm, (4.44), 231 (4.85), 274 (4.75). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.52 (dd, $J_{gem.}$ = 12.1 Hz, $J_{6,5}$ = 5.3 Hz, 1 H, H-6), 4.75–4.96 (m, 1 H, H-5), 5.00–5.31 (m, 31 H, H-6, OCH_2Ph), 5.80 (dd, $J_{2,1}$ = 3.6 Hz, $J_{2,3}$ = 10.1 Hz, 1 H,

H-2), 5.96 (t, $J_{4,3}$ = 10.0 Hz, $J_{4,5}$ = 10.1 Hz, 1 H, H-4), 6.55 (t, $J_{3,2}$ = 10.1 Hz, $J_{3,4}$ = 10.0 Hz, 1 H, H-3), 7.02 (d, $J_{1,2}$ = 3.6 Hz, 1 H, H-1), 7.30–7.66 (m, 85 H, H-Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 62.78 (t, C-6), 69.61 (d, C-4), 70.62 (d, C-5), 70.77 (d, C-2 and C-3), 70.90, 70.97, 71.03 and 71.23 (t, OCH_2Ph), 75.00, 75.03 and 75.07 (t, OCH_2Ph), 90.23 (d, C-1), 109.03, 109.09, 109.12, 109.33 and 109.39 (d, Gall-C-2 and Gall-C-6), 123.44, 123.62, 123.72 and 124.45 (s, Gall-C-1), 127.46, 127.56, 127.78, 127.93, 127.95, 128.04, 128.07, 128.15, 128.20, 128.24, 128.34, 128.40, 128.47 and 128.52 (d, C-Ar), 136.12, 136.18, 136.21, 136.32, 136.56, 137.24 and 137.39 (s, C-Ar), 142.64, 142.98, 143.06, 143.24 and 143.43 (s, Gall-C-4), 152.42, 152.46, 152.55 and 152.61 (s, Gall-C-3 and Gall-C-5), 163.91, 164.85, 165.13, 165.57 and 165.84 (s, COOR). – Analysis: $C_{146}H_{122}O_{26}$ (2292.54) calcd. C 76.49 H 5.36 found C 76.40 H 5.46. **β-anomer:** $[\alpha]_D^{20}$ = –1.0° (c = 0.4, CH_2Cl_2). – IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1} (aromat. CH), 3030 (aromat. CH), 2933 (aliphat. CH), 2868 (aliphat. CH), 1728 (CO, ester), 1585 (aromat. CC), 1500 (aromat. CC), 1429, 1334, 1196, 1113. – UV (CH_2Cl_2): λ_{max} (lg ε) = 231 nm (4.78), 276 (4.67). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.52–4.65 (m, 2 H, H-5, H-6), 4.98 (d, J_{gem} = 10.9 Hz, 1 H, H-6), 5.08–5.32 (m, 30 H, OCH_2Ph), 5.94 (t, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 6.03 (t, $J_{2,1}$ = 8.1 Hz, $J_{2,3}$ = 9.5 Hz, 1 H, H-2), 6.27 (t, $J_{3,2}$ = 9.5 Hz, $J_{3,4}$ = 9.5 Hz, 1 H, H-3), 6.43 (d, $J_{1,2}$ = 8.1 Hz, 1 H, H-1), 7.30–7.62 (m, 85 H, H-Ar). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 63.74 (t, C-6), 70.36 (d, C-4), 71.52, 71.58, 71.67 and 71.75 (t, OCH_2Ph), 73.82 (d, C-3 and C-5), 75.66 (t, OCH_2Ph), 77.85 (d, C-2), 93.58 (d, C-1), 109.62, 109.67, 109.80 and 109.86 (d, Gall-C-2 and Gall-C-6), 123.88, 124.14, 124.24 and 125.11 (s, Gall-C-1), 128.10, 128.17, 128.42, 128.46, 128.60, 128.71, 128.79, 128.87, 128.96, 129.01, 129.02, 129.07 and 129.09 (d, C-Ar), 136.85, 136.92, 136.98, 137.26, 137.86, 137.90 and 138.04 (s, C-Ar), 143.10, 143.62, 143.67 and 143.72 (s, Gall-C-4), 153.02, 153.12 and 153.16 (s, Gall-C-3 and Gall-C-5), 164.79, 165.57, 165.62, 166.16 and 166.24 (s, COOR). – Analysis: $C_{146}H_{122}O_{26}$ (2292.54) calcd. C 76.49 H 5.36 found C 76.41 H 5.44.

1,2,3,4,6-Penta-O-galloyl-β-D-glucopyranose (**10**): A suspension of **9** (0.14 g, 0.06 mmol) in dry THF (20 ml) was treated with hydrogen, according to the general procedure B, to give an oil. Reversed phase chromatography (H_2O/MeOH, 80:50) gave **10** (51 mg, 89%) as a yellow powder, dec. >250 °C, $[\alpha]_D^{20}$ = +18.5° (c = 0.4, acetone); Lit.:[23] $[\alpha]_D^{20}$ = +18.2° (c = 1.0, acetone). It had no m.p. < 250 °C. – IR (KBr): $\tilde{\nu}$ = 3416 cm^{-1} (OH and aromat. CH), 2960 (aliphat. CH), 2925 (aliphat. CH), 1707 (CO, ester), 1718 (CO, ester), 1734 (CO, ester), 1687, 1630 (aromat. CC), 1466, 1448, 1317, 1201. – UV (EtOAc): λ_{max} (lg ε) = 229 nm (4.83), 282 (4.92). – ^{1}H NMR (300 MHz, acetone-d_6/D_2O): δ = 4.56–4.74 (m, 3 H, H-5, H-6), 5.61 (t, $J_{2,1}$ = 8.2 Hz, $J_{2,3}$ = 9.6 Hz, 1 H, H-2), 5.65 (t, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 9.6 Hz, 1 H, H-4), 5.98 (t, $J_{3,2}$ = 9.6 Hz, $J_{3,4}$ = 9.5 Hz, 1 H, H-3), 6.24 (d, $J_{1,2}$ = 8.2 Hz, 1 H, H-1), 6.94, 6.97, 7.01, 7.04 and 7.10 (s, 10 H, Gall-H-2 and Gall-H-6). – ^{13}C NMR (75 MHz, acetone-d_6/D_2O): δ = 62.67 (t, C-6), 69.04 (d, C-4), 71.42 (d, C-2), 73.01 (d, C-3), 73.34 (d, C-5), 93.01 (d, C-1), 109.80, 109.90 and 110.02 (d, Gall-C-2 and Gall-C-6), 118.80, 119.33, 119.40, 119.45 and 120.36 (s, Gall-C-1), 138.99, 139.27, 139.43 and 139.84 (s, Gall-C-4), 145.55, 145.64 and 145.76 (s, Gall-C-3 and Gall-C-5), 165.28, 165.98, 166.17, 166.35 and 166.78 (s, COOR). – MS (FAB/glycerine, neg.): m/z (%) = 940 (6) [M^+], 786 (4), 601 (6), 447 (8), 391 (10), 277 (52), 183 (86), 169 (100), 127 (46). – Analysis: $C_{41}H_{32}O_{26}$ (940.68) calcd. C 52.35 H 4.43 found C 52.11 H 4.56.

1,2,3,4,6-Penta-O-galloyl-α-D-glucopyranose (**13**): A suspension of **12** (0.14 g, 0.06 mmol) in dry THF (20 ml) was treated with hydrogen, according to the general procedure B, to give an oil. Reversed phase chromatography (H_2O/MeOH, 80:50) gave **13** (52 mg, 90 %) as a yellow powder, dec. >210 °C. $[\alpha]_D^{20}$ = +63.0° (c = 0.4, acetone). – IR (KBr): $\tilde{\nu}$ = 3417 cm^{-1} (OH and aromat. CH), 2960 (aliphat. CH), 2924 (aliphat. CH), 1701 (CO, ester), 1718 (CO, ester), 1685, 1610 (aromat. CC), 1541 (aromat.CC), 1535 (aromat. CC), 1448, 1334, 1321, 1205. – UV (EtOAc): λ_{max} (lg ε) = 221 nm (4.79), 281 (4.55). – ^{1}H NMR (300 MHz, acetone-d_6/D_2O): δ = 4.27–4.33 (m, 1 H, H-6), 4.56–4.60 (m, 1 H, H-6), 4.65–4.68 (m, 1 H, H-5), 5.47 (dd, $J_{2,1}$ = 3.7 Hz, $J_{2,3}$ = 10.0 Hz, 1 H, H-2), 5.78 (t, $J_{4,3}$ = 10.0 Hz, $J_{4,5}$ = 10.0 Hz, 1 H, H-4), 6.19 (t, $J_{3,2}$ = 10.0 Hz, $J_{3,4}$ = 10.0 Hz, 1 H, H-3), 6.67 (d, $J_{1,2}$ = 3.7 Hz, 1 H, H-1), 6.96, 7.00, 7.05, 7.14 and 7.24 (s, 10 H, Gall- H-2 and Gall-H-6). – ^{13}C NMR (75 MHz, acetone-d_6/D_2O): δ = 62.39 (t, C-6), 68.67 (d, C-4), 70.80 (d, C-5), 71.13 (d, C-2 and C-3), 89.98 (d, C-1), 109.84, 109.98 and 110.08 (d, Gall-C-2 and Gal-C-6), 119.33, 119.56, 119.71 and 120.56 (s, Gall-C-1), 139.03, 139.34, 139.43, 139.50 and 139.80 (s, Gall-C-4), 142.45, 145.70, 145.75, 145.79 and 146.01 (s, Gall-C-3 and Gall-C-5), 165.15, 166.00 and 166.13 (s, COOR), 166.72 (s, 2 x COOR). - MS (FAB/glycerine, neg.): m/z (%) = 940 (14) [M^+], 786 (7), 601 (14), 465 (8), 391 (24), 277 (66), 183 (46), 169 (100), 124 (44). – Analysis: $C_{41}H_{32}O_{26}$ (940.68) calcd. C 52.35 H 4.43 found C 52.13 H 4.58.

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