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Note

Improved synthesis of substituted 2,6-dioxabicyclo[3.1.1]heptanes: 1,3-anhydro-2,4,6-tri-*O*-benzyl-2,4,6-tri-*O*-*p*-bromobenzyl- and -2,4,6-tri-*O*-*p*-methylbenzyl-β-D-glucopyranose

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The syntheses of 1,3-anhydro-2,4,6-tri-*O*-benzyl- (**15**), 2,4,6-tri-*O*-(*p*-bromobenzyl)- (**16**), and 2,4,6-tri-*O*-(*p*-methylbenzyl)-β-D-glucopyranose (**17**) are of interest as their stereospecific polymerization would yield a (1→3)-α-D-glucopyranan. Such glucopyranans are prominent components of the cell walls of bacteria, yeast, fungi, and lichens[1a–q].

The previous synthesis of a substituted 1,3-anhydro-β-D-glucopyranose[2] had several difficulties. After benzylation of allyl 3-*O*-allyl-D-glucopyranoside, rearrangement of the allyl groups with potassium *tert*-butoxide in boiling toluene tended to give equilibrium mixtures of allyl and propenyl derivatives rather than complete conversion into propenyl derivatives. Conversion of 2,4,6-tri-*O*-benzyl-D-glucopyranose into the corresponding glucopyranosyl chloride led to the formation of a (1→3)-linked disaccharide that was difficult to separate from the desired product. The by-product of the subsequent ring closure reaction, a glucal derivative, made purification of the 1,3-anhydroglucopyranose difficult. The present method constitutes an improved synthesis of substituted 1,3-anhydro-β-D-glucopyranoses.

Allyl 3-*O*-allyl-D-glucopyranoside (**2**) was prepared, in good yield, by the direct allyl glycosidation of 3-*O*-allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[3] (**1**). Benzylation, *p*-bromobenzylation, or *p*-methylbenzylation afforded allyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl- (**3**), 2,4,6-tri-*O*-(*p*-bromobenzyl)- (**4**), and 2,4,6-tri-*O*-(*p*-methylbenzyl)-D-glucopyranoside (**5**). The by-products of benzylation, dibenzyl ethers, were difficult to separate from the desired products by liquid chromatography, as they had retention times similar to those of compounds **3**, **4**, and **5**. The dibenzyl ethers also inhibited crystallization of these compounds. Therefore, compounds **3**, **4**, and **5** were not isolated, but were deallylated directly, with chlorotris(triphenylphosphine)rhodium[4], to give 2,4,6-tri-*O*-benzyl- (**6**), 2,4,6-tri-

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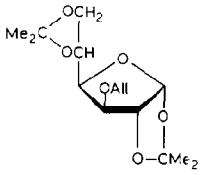
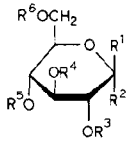
O-(*p*-bromobenzyl)- (**7**), and 2,4,6-tri-*O*-(*p*-methylbenzyl)-D-glucopyranose (**8**), whose n.m.r. spectra showed no resonances from allyl or propenyl groups. Acetylation of **6**, **7**, and **8** gave, respectively, 1,3-di-*O*-acetyl-2,4,6-tri-*O*-benzyl- (**9**), 2,4,6-tri-*O*-(*p*-bromobenzyl)- (**10**), and 2,4,6-tri-*O*-(*p*-methylbenzyl)-β-D-glucopyranose (**11**) in quantitative yields. Treatment with anhydrous hydrogen chloride, by the method of Micheel and Kreutzer[5], converted **9**, **10**, and **11** into 3-*O*-acetyl-2,4,6-tri-*O*-benzyl- (**12**), 2,4,6-tri-*O*-(*p*-bromobenzyl)- (**13**), and 2,4,6-tri-*O*-(*p*-methylbenzyl)-α-D-glucopyranosyl chloride (**14**). The glucosyl chlorides formed by this method were stable and crystalline.

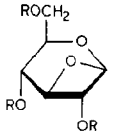


1



2-14

2 R^1, R^2 = H, OAlly, R^4 = Allyl, R^3, R^5, R^6 = H
3 R^1, R^2 = H, OAlly, R^4 = Allyl, R^3, R^5, R^6 = Bzl
4 R^1, R^2 = H, OAlly, R^4 = Allyl, R^3, R^5, R^6 = p-$BrC_6H_4CH_2$
5 R^1, R^2 = H, OAlly, R^4 = Allyl, R^3, R^5, R^6 = p-$CH_3C_6H_4CH_2$
6 R^1, R^2 = H, OH, R^4 = H, R^3, R^5, R^6 = Bzl
7 R^1, R^2 = H, OH, R^4 = H, R^3, R^5, R^6 = p-$BrC_6H_4CH_2$
8 R^1, R^2 = H, OH, R^4 = H, R^3, R^5, R^6 = p-$MeC_6H_4CH_2$
9 R^1 = OAc, R^2 = H, R^4 = Ac, R^3, R^5, R^6 = Bzl
10 R^1 = OAc, R^2 = H, R^4 = Ac, R^3, R^5, R^6 = p-$BrC_6H_4CH_2$
11 R^1 = OAc, R^2 = H, R^4 = Ac, R^3, R^5, R^6 = p-$MeC_6H_4CH_2$
12 R^1 = H, R^2 = Cl, R^4 = Ac, R^3, R^5, R^6 = Bzl
13 R^1 = H, R^2 = Cl, R^4 = Ac, R^3, R^5, R^6 = p-$BrC_6H_4CH_2$
14 R^1 = H, R^2 = Cl, R^4 = Ac, R^3, R^5, R^6 = p-$MeC_6H_4CH_2$



15-17

15 R = Bzl
16 R = p-$BrC_6H_4CH_2$
17 R = p-$MeC_6H_4CH_2$

Ring-closure experiments were performed under various conditions. When **12**, **13**, or **14** was treated with potassium *tert*-butoxide, in oxolane or 1,2-dimethoxyethane, the main product was a glucal derivative produced by *trans*-diaxial

elimination of hydrogen chloride from C-1 and C-2. The highest yields of **15**, **16**, and **17** were obtained by treatment of **12**, **13**, or **14** with lithium ethoxide (generated *in situ* from methyllithium and abs. ethanol) in refluxing oxolane. Formation of a glucal derivative was minimized, and no ethyl glucoside could be detected (analytical l.c. and ^{1}H-n.m.r.).

EXPERIMENTAL

General methods. — These were as described in ref. 2.

Allyl 3-O-allyl-D-glucopyranoside (**2**). — Strongly acidic cation-exchange resin (Dowex 50X8, 200–400 mesh, 45 g), allyl alcohol (850 mL, 12.5 mol), and 3-*O*-allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**, 127 g, 0.42 mol) were placed in a 2-L round-bottomed flask. The reaction, monitored by t.l.c. (4:1 chloroform–methanol), was judged complete after boiling for 2 h under reflux. The mixture was allowed to cool, filtered, and the resin washed with allyl alcohol. Removal of the solvent under vacuum left a syrup. The product was purified by preparative l.c. (pure ethyl acetate); yield 77%. Compound **2** gave spectra the same as recorded in the literature[2].

2,4,6-Tri-O-(p-bromobenzyl)-D-glucopyranose (**7**). — Allyl 3-*O*-allyl-2,4,6-tri-*O*-(*p*-bromobenzyl)-D-glucopyranoside (63 g, 82 mmol), prepared by *p*-bromobenzylation of allyl 3-*O*-allyl-D-glucopyranoside (22 g, 85 mmol) with *p*-bromobenzyl bromide (75 g, 0.30 mol) and sodium hydride (11 g, 0.28 mol, 60% oil dispersion) in boiling oxolane (100 mL), was dissolved in benzene (100 mL)–aqueous ethanol (400 mL). Chlorotris(triphenylphosphine)rhodium (800 mg, 0.865 mmol) was added, and the solution was boiled overnight under reflux. The solvent was evaporated under vacuum. The resulting syrup was purified by preparative l.c. (1:2 ethyl acetate–hexanes), crystallized from ethyl acetate–hexanes, and recrystallized from ethyl acetate; yield 80%; m.p. 133–134°, $[\alpha]_D^{25}$ +40.6° (*c* 1.02, chloroform, equil.); ^{1}H-n.m.r. ($CDCl_3$): δ 7.5–6.9 (12 H, m, aromatic), 5.2–2.7 [15 H, m, H-1, 3 $CH_2C_6H_4Br$, (2) H-6, H-2,3,4,5, (2) OH]; ^{13}C-n.m.r. ($CDCl_3$): α anomer: 90.83 (C-1), 79.95 (C-2); β anomer: 97.32 (C-1) and 84.42 (C-2).

Anal. Calc. for $C_{27}H_{27}Br_3O_6$: C, 47.17; H, 3.96. Found: C, 47.42; H, 3.80.

2,4,6-Tri-O-(p-methylbenzyl)-D-glucopyranose (**8**). — Allyl 3-*O*-allyl-2,4,6-tri-*O*-(*p*-methylbenzyl)-D-glucopyranoside (40 g, 70 mmol), prepared by *p*-methylbenzylation of allyl 3-*O*-allyl-D-glucopyranoside (21 g, 81 mmol) with *p*-methylbenzyl chloride (90 mL, 0.68 mol) and sodium hydride (12.0 g, 0.30 mol, 60% oil dispersion) in boiling toluene, was dissolved in toluene (100 mL)–aqueous ethanol (200 mL). After the addition of chlorotris(triphenylphosphine)rhodium (1.3 g, 1.4 mmol) the solution was boiled for 48 h under reflux. The solvent was removed under diminished pressure. The product was purified by preparative l.c. (1:2 ethyl acetate–hexanes), crystallized from ethanol–hexanes, and recrystallized from ethyl acetate–hexanes; yield 80%; m.p. 79.5–80.5°, $[\alpha]_D^{25}$ +37.0° (*c* 0.97, chloroform, equil.); ^{1}H-n.m.r. ($CDCl_3$): δ 7.3–6.9 (12 H, m, aromatic), 5.15–3.2 [15 H, m, 3

$CH_2C_6H_4CH_3$, (2) H-6, H-1,2,3,4,5, (2) OH], 2.25 (9 H, s, 3 $CH_3C_6H_4CH_2$); ^{13}C-n.m.r. ($CDCl_3$): α anomer: 90.86 (C-1), 79.63 (C-2), 68.77 (C-6), β anomer: 97.30 (C-1), 82.33 (C-2), and 69.04 (C-6).

Anal. Calc. for $C_{30}H_{36}O_6$: C, 73.14; H, 6.96. Found: C, 73.21; H, 7.06.

1,3-Di-O-acetyl-2,4,6-tri-O-benzyl-β-D-glucopyranose (**9**). — 2,4,6-Tri-*O*-benzyl-D-glucopyranose[2] (**6**, 4.2 g, 9.3 mmol, m.p. 85–86°) was dissolved in dichloromethane (20 mL) and triethylamine (7.5 mL, 54 mmol). After addition of acetic anhydride (4.5 mL, 48 mmol), the solution was stirred for 6 h at room temperature. T.l.c. (1:2 ethyl acetate–hexanes) showed that the reaction had gone to completion. After conventional processing, compound **9** was crystallized from diethyl ether and recrystallized from ethyl acetate–hexanes; yield quantitative; m.p. 112–113.5°, $[\alpha]_D^{25}$ +19.8° (*c* 0.99, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.4–7.0 (15 H, m, aromatic), 5.65 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.3 (1 H, d of d, $J_{2,3} \approx J_{3,4} \approx 9$ Hz, H-3), 4.9–4.3 (6 H, m, 3 CH_2Ph), 3.95–3.35 [5 H, m, (2) H-6, H-2,4,5], 2.05 (3 H, s, 1-OAc), 1.8 (3 H, s, 3-OAc); ^{13}C-n.m.r. ($CDCl_3$): 169.96, 169.13 (C=O), 138.09 (aromatic C-1), 128.60, 128.19, 128.00 (aromatic C), 94.22 (C-1), 78.68 (C-2), 75.75, 75.51, 74.40, 73.73 (C-3,4,5, 3 OCH_2), 68.08 (C-6), and 20.96 (CH_3C=O).

Anal. Calc. for $C_{31}H_{34}O_8$: C, 69.65; H, 6.41. Found: C, 69.62; H, 6.54.

1,3-Di-O-acetyl-2,4,6-tri-O-(p-bromobenzyl)-β-D-glucopyranose (**10**). — Compound **7** (8.4 g, 10.9 mmol) was dissolved in dichloromethane (30 mL) and triethylamine (11 mL, 79 mmol). After addition of acetic anhydride (7.5 mL, 79.5 mmol), the solution was boiled for 48 h under reflux. Analytical t.l.c. (1:3 ethyl acetate–hexanes) and ^{1}H-n.m.r. showed the reaction to be complete. After conventional processing, the diacetate **10** was crystallized from diethyl ether and recrystallized from ethyl acetate–hexanes; yield quantitative; m.p. 84.5–85°, $[\alpha]_D^{25}$ +23.1° (*c* 0.97, chloroform) ^{1}H-n.m.r. ($CDCl_3$): δ 7.6–6.9 (12 H, m, aromatic), 5.65 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.25 (1 H, d of d, $J_{2,3} \approx J_{3,4} \approx 8$ Hz, H-3), 4.7–4.3 (6 H, m, 3 $CH_2C_6H_4Br$), 3.8–3.2 [5 H, m, (2) H-6, H-2,4,5], 2.1 (3 H, s, 1-OAc), 1.9 (3 H, s, 3-OAc); ^{13}C-n.m.r. ($CDCl_3$): 169.79, 169.00 (C=O), 137.07, 136.95 (aromatic C-1), 131.75, 129.73, 129.44 (aromatic C), 122.19, 121.93 (aromatic C-4), 94.04 (C-1), 78.83 (C-2), 75.81, 75.63, 75.33, 73.53, 72.91 (C-3,4,5, 3 OCH_2), 68.17 (C-6), and 20.93 (CH_3C=O).

Anal. Calc. for $C_{31}H_{31}Br_3O_8$: C, 48.25; H, 4.05. Found: C, 48.43; H, 4.19.

1,3-Di-O-acetyl-2,4,6-tri-O-(p-methylbenzyl)-β-D-glucopyranose. (**11**). — Compound **8** (3.0 g, 6.1 mmol) was acetylated by the procedure used to convert **7** into **10**. The product **11** was crystallized from diethyl ether, and recrystallized from ethyl acetate–hexanes; yield quantitative; m.p. 71.5–72°, $[\alpha]_D^{25}$ +19.5° (*c* 1.05, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.3–6.8 (12 H, m, aromatic), 5.5 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.2 (1 H, d of d, $J_{2,3} \approx J_{3,4} \approx 9$ Hz, H-3), 4.9–4.2 (6 H, m, 3 $CH_2C_6H_4CH_3$), 3.7–3.2 [5 H, m, (2) H-6, H-2,4,5], 2.3 (9 H, s, 3 $CH_3C_6H_4CH_2$), 2.05 (3 H, s, 1-OAc), 1.8 (3 H, s, 3-OAc); ^{13}C-n.m.r. ($CDCl_3$): 169.96, 169.19 (C=O), 137.72 (aromatic C-1), 135.15 (aromatic C-4), 129.30, 128.48, 128.19

(aromatic C), 94.29 (C-1), 78.43 (C-2), 75.92, 75.57, 74.29, 73.64 (C-3,4,5, 3 OCH_2), 67.87 (C-6), 21.16 ($CH_3C_6H_4CH_2$), and 21.04 ($CH_3C{=}O$).

Anal. Calc. for $C_{34}H_{40}O_8$: C, 70.81; H, 6.99. Found: C, 71.31; H, 7.07.

3-O-Acetyl-2,4,6-tri-O-benzyl-α-D-glucopyranosyl chloride (**12**). — The 1,3-diacetate **9** (1.1 g, 2.1 mmol) was dissolved in dry ethyl ether (40 mL). Under nitrogen flow, the solution was saturated with anhydrous hydrogen chloride at 0°. After 18 h at room temperature, t.l.c. (1:2 ethyl acetate–hexanes) showed the reaction to be complete. Nitrogen was bubbled into solution to remove the excess of hydrogen chloride. The solution was evaporated. The product was purified by analytical l.c. (19:1 dichloromethane–ethyl acetate), and crystallized from carbon tetrachloride–hexanes; yield 99%; m.p. 73.5–74°, $[\alpha]_D^{25}$ +90.8° (*c* 0.98, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.25 (15 H, d, aromatic), 6.1 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1), 5.6 (1 H, d of d, $J_{2,3} \approx J_{3,4} \approx 9.5$ Hz, H-3), 4.5 (6 H, s, 3 CH_2Ph), 4.3–3.5 [5 H, m, (2) H-6, H-2,4,5], 1.9 (3 H, s, OAc); ^{13}C-n.m.r. ($CDCl_3$): 169.87 (C=O), 137.99, 137.89, 137.53 (aromatic C-1), 128.67, 128.24, 128.05 (aromatic C), 92.72 (C-1), 77.51 (C-2), 75.20 (C-4), 74.60, 73.76, 73.29, 73.10, 72.59 (C-3,5, 3 OCH_2), 67.80 (C-6), and 20.96 ($CH_3C{=}O$).

Anal. Calc. for $C_{29}H_{31}ClO_6$: C, 68.16; H, 6.11. Found: C, 68.10; H, 5.96.

3-O-Acetyl-2,4,6-tri-O-(p-bromobenzyl)-α-D-glucopyranosyl chloride (**13**). — Compound **10** (9.7 g, 13.0 mmol) was dissolved in a mixture of diethyl ether (110 mL) and dichloromethane (15 mL). Conversion into compound **13** was accomplished by the same procedure used to convert **9** into **12**. After purification on an open column of silica gel with dichloromethane as eluant, the product **13** crystallized from carbon tetrachloride–hexanes; yield 89%; m.p. 56.5–58°, $[\alpha]_D^{25}$ +72.4° (*c* 1.05, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.6–6.9 (12 H, m, aromatic), 6.1 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1), 5.5 (1 H, d of d, $J_{2,3} \approx J_{3,4} \approx 9$ Hz, H-3), 4.75–3.4 [11 H, m, 3 $CH_2C_6H_4Br$, (2) H-6, H-2,4,5], 1.95 (3 H, s, OAc); ^{13}C-n.m.r. ($CDCl_3$): 169.67 (C=O), 136.99, 136.60 (aromatic C-1), 131.94, 129.80, 129.50 (aromatic C), 122.33, 122.14 (aromatic C-4), 92.33 (C-1), 77.90 (C-2), 75.38, 73.72, 73.24, 73.06, 71.87 (C-3,4,5, 3 OCH_2), 68.00 (C-6), and 20.94 ($CH_3C{=}O$).

Anal. Calc. for $C_{29}H_{28}Br_3ClO_6$: C, 46.56; H, 3.77. Found: C, 46.41; H, 3.68.

3-O-Acetyl-2,4,6-tri-O-(p-methylbenzyl)-α-D-glucopyranosyl chloride (**14**). — The diacetate **11** (3.6 g, 6.2 mmol) was converted into the corresponding glucosyl chloride **14** by the procedure used to convert **10** into **13**. Compound **14** crystallized from carbon tetrachloride–hexanes; yield 95%; m.p. 72–74°, $[\alpha]_D^{25}$ +84.6° (*c* 1.17, chloroform), ^{1}H-n.m.r. ($CDCl_3$): δ 7.05 (12 H, d, aromatic), 6.0 (1 H, d, $J_{1,2}$ 4 Hz, H-1), 5.5 (1 H, d of d, $J_{2,3} \approx J_{3,4} \approx 9$ Hz, H-3), 4.4 (6 H, d, 3 $CH_2C_6H_4CH_3$), 4.0–3.4 [5 H, m, (2) H-6, H-2,4,5], 2.3 (9 H, s, 3 $CH_3C_6H_4CH_2$), 1.9 (3 H, s, $CH_3C{=}O$); ^{13}C-n.m.r. ($CDCl_3$): 169.85 (C=O), 138.09, 137.84, 137.73, 135.05, 134.86, 134.53 (aromatic C-1,4), 129.39, 128.45, 128.18 (aromatic C), 92.86 (C-1), 77.25 (C-2), 75.03, 74.11, 73.60, 73.30, 72.49 (C-3,4,5, 3 OCH_2), 67.58 (C-6), 21.15 ($CH_3C_6H_4CH_2$), and 20.93 ($CH_3C{=}O$).

Anal. Calc. for $C_{29}H_{31}ClO_6$: C, 68.16; H, 6.11. Found: C, 68.10; H, 5.96.

*1,3-Anhydro-2,4,6-tri-*O*-benzyl-β-*D*-glucopyranose* (**15**). — Methyllithium (0.25 mL, 1.55 m in ethyl ether, 0.40 mmol), in dry oxolane (100 mL), was treated with abs. ethanol (23 μL, 0.40 mmol) under a flow of nitrogen. The solution was brought to boiling under reflux and then a solution of **12** (100 mg, 0.20 mmol) in oxolane (2 mL) was added dropwise. The reaction was allowed to proceed at the same temperature for an additional 24 h. Analytical l.c. (2:5 ethyl acetate–hexanes) showed the reaction to be complete. The product was concentrated to a syrup, redissolved in 1:2 ethyl acetate–hexanes and the mixture filtered. After removal of the solvent, compound **15** was purified by analytical l.c. (2:5 ethyl acetate–hexanes); yield 95%; $[\alpha]_D^{25}$ +59.2° (*c*0.95, chloroform); lit.[2] $[\alpha]_D^{25}$ +58.0° (*c* 1, chloroform). Compound **15** gave spectra the same as those recorded in the literature[2].

*1,3-Anhydro-2,4,6-tri-*O*-(p-bromobenzyl)-β-*D*-glucopyranose* (**16**). — Compound **13** (1.0 g, 1.3 mmol) was converted into **16** by the procedure used to convert **12** into **15**. After 30 h, analytical l.c. and ^{1}H-n.m.r. showed the reaction to be complete. The product (**16**) was concentrated to a syrup, redissolved in dichlormethane, and the solution washed with water. The organic phase was dried over anhydrous sodium sulfate, and concentrated under vacuum. Compound **16** was purified by analytical l.c. using 1:3 ethyl acetate–hexanes as eluant, and crystallized from ethyl acetates–hexanes; yield 92%; m.p. 76–77°, $[\alpha]_D^{25}$ +64.7° (*c* 1.36, chloroform; ^{1}H-n.m.r. ($CDCl_3$): δ 7.55–6.9 (12 H, m, aromatic), 5.45 (1 H, d of d, $^3J_{1,2} \approx {}^4J_{1,3} \approx 3.8$ Hz, H-1), 4.8–3.8 (10 H, m, 3 $CH_2C_6H_4Br$, H-2,3,4,5), 3.5 [2 H, d, (2) H-6]; ^{13}C-n.m.r. ($CDCl_3$): 137.43, 137.12, 136.53 (aromatic C-1), 131.64, 129.50 (aromatic C), 121.92, 121.52 (aromatic C-4), 106.08 (C-1), 80.81 (C-3), 76.40, 74.80, 72.76, 72.58, 71.60, and 70.82 (C-2,4,5,6, 3 OCH_2).

Anal. Calc. for $C_{27}H_{25}Br_3O_5$: C, 48.44; H, 3.76. Found: C, 48.13; H, 3.81.

*1,3-Anhydro-2,4,6-tri-*O*-(p-methylbenzyl)-β-*D*-glucopyranose* (**17**). — Compound **14** (0.87 g, 1.6 mmol) was converted into **17** by the same procedure used to convert **12** into **15**. Purification by analytical l.c. (1:3 ethyl acetate–hexanes) afforded syrupy **17**; yield 92%; $[\alpha]_D^{25}$ +56.1° (*c* 1.23, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.1 (12 H, d, aromatic), 5.4 (1 H, d of d, $^3J_{1,2} \approx {}^4J_{1,3} \approx 3.8$ Hz, H-1), 4.8–3.8 (10 H, m, 3 $CH_2C_6H_4CH_3$, H-2,3,4,5), 3.5 [2 H, d, (2) H-6], 2.3 (9 H, s, 3 $CH_3C_6H_4CH_2$); ^{13}C-n.m.r. ($CDCl_3$): 137.57, 137.18, 135.69, 135.56, 134.81 (aromatic C-1,4), 129.26, 128.18 (aromatic C), 106.35 (C-1), 81.19 (C-3), 76.66, 74.84, 73.27, 72.73, 72.37, 71.47 (C-2,4,5,6, 3 OCH_2), and 21.15 ($CH_3C_6H_4CH_2$).

Anal. Calc for $C_{30}H_{34}O_5$: C, 75.92; H, 7.22. Found: C, 76.65; H, 7.06.

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