Diastereoselective Free-Radical Reactions. Part 2.† Synthesis of 2-Deoxy-β-*C*-pyranosides by Diastereoselective Hydrogen-Atom Transfer

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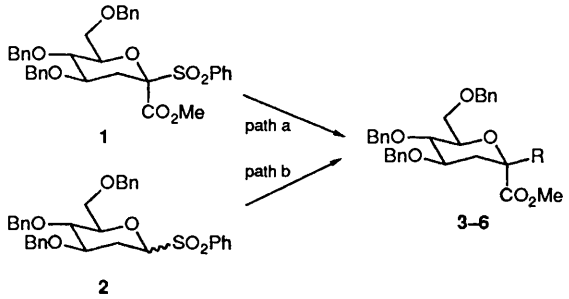
C-Glycosides of 2,3-dideoxy-*arabino*-heptulosonate esters are prepared from the corresponding 2,3-dideoxy-1-phenylsulphonyl derivatives by reductive desulphonylation with lithium naphthalenide and quenching of the so-formed enolate with appropriate alkyl halides. These *C*-glycosides are saponified and decarboxylated by the Barton *O*-acyl thiohydroxamate protocol to give 2-deoxy-β-*C*-glycosides with very high diastereoselectivities.

Diastereoselectivity in free-radical reactions is an area of considerable current interest[1] with remarkable progress having been made recently in the acyclic stereoselection field by the Curran,[2] Giese[3] and Porter[4] groups. One area of particular interest is that of face selectivity in the quenching of glycos-1-yl (or anomeric) radicals. For example, the 2,3,4,6-tetraacetates of both the glucopyranos-1-yl and the mannopyranos-1-yl radicals are quenched with high selectivity from the α-face by standard radical traps.[5] Good face selectivity is also obtained under certain conditions with anomeric furanosyl radicals.[6] The majority of these reactions rely on the quenching of the anomeric radical with a carbon–carbon multiple bond, resulting in the formation of α-*C*-glycopyranosides. In this laboratory we have adopted an alternative approach in which the required functionality is introduced by polar mechanisms prior to the radical step. The functionalised glycosyl radical is then quenched, from the α-face, by hydrogen-atom transfer from a suitable hydrogen-atom donor, resulting in the formation of β-glycosidic linkages. Specifically we have successfully applied this concept to the generation of the otherwise difficulty accessible 2-deoxy-β-glycosides.[7,8] Herein we describe, in full, the extension of this approach to the highly selective preparation of 2-deoxy-β-*C*-glucosides.[9] A related approach, involving alkylation of 1-nitro glycosides and subsequent reductive denitration, has been described by the Vasella group.[10] The approach to β-*C*-glycosides described in this paper may be viewed as a radical alternative to the method of Kishi involving nucleophilic attack on aldonolactones followed by Lewis acid-mediated reduction with triethylsilane.[11]



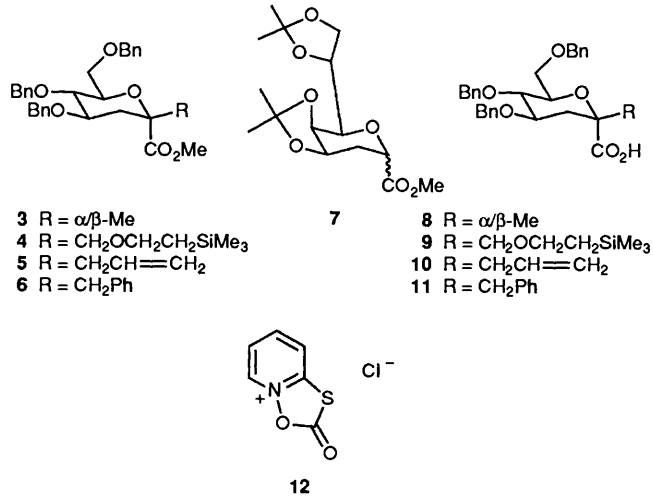
Scheme 1 Path a: i, LN; ii, RX. Path b: i, LDA; ii, $MeOCO_2Me$; iii, LN; iv, RX

The appropriate radical precursors (**3**–**6**) were prepared in the first instance by treatment of the sulphone ester **1** with lithium naphthalenide (LN) in tetrahydrofuran (THF) followed by the requisite alkyl halide (Table 1, entries 1 and 2; Scheme 1, path a). With the exception of the use of methyl iodide as electrophile essentially single anomers were obtained. The configuration of these products was not assigned rigorously but was assumed to be as illustrated on stereoelectronic grounds and on the basis of comparison with related work by the Claesson group on the alkylation of the ester **7**.[12] Subsequent esters were prepared by a two-step, one-pot, procedure from the sulphone **2** by sequential treatment with lithium diisopropylamide (LDA), dimethyl carbonate, LN, and the alkyl halide (Table 1, entries 3 and 4; Scheme 1, path b). We note, in passing, the use of β-(trimethylsilyl)ethoxy methyl chloride as a convenient alternative to the use of gaseous formaldehyde for the introduction of a protected hydroxymethyl residue.[13]

Table 1 Formation of radical precursors

Entry	Method[a]	Alkyl halide	Product (% Yield)
1	a	MeI	**3** (50)
2	a	$MeSiCH_2CH_2OCH_2Cl$	**4** (70)
3	b	$CH_2{=}CHCH_2Br$	**5** (44)
4	b	$PhCH_2Br$	**6** (56)

[a] a Scheme 1, Path a; b Scheme 1, Path b.



Esters **3**–**6** were then saponified by standard methods to give the corresponding acids **8**–**11**, which were then caused to undergo reductive radical-chain decarboxylation by the Barton *O*-acyl thiohydroxamate methodology.[14] In accordance with our earlier work[7] on the preparation of 2-deoxy-β-glycosides

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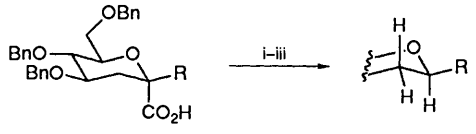
Table 2 Reductive decarboxylation of ulosonic acids

Entry	Ester	Intermediate acid (% yield)	Product (% yield)
1	**3**	**8** (88)	**13** (56)
2	**4**	**9** (82)	**14** (58)
3	**5**	**10** (77)	**15** (73)
4	**6**	**11** (72)	**16** (92)

we chose the reaction of the acids in the form of their triethylammonium salts with the heterocyclic salt **12** for the formation of the all-important *O*-acyl thiohydroxamates followed by their immediate *in situ* photolysis in the presence of a tertiary thiol as the optimum version of this methodology for small-scale work with sensitive molecules. Commercial *t*-dodecanethiol, a mixture of isomers, was chosen as the thiol on grounds both of availability and relative inoffensiveness. In the event, in each of the four cases studied (Table 2), moderate-to-good yields of the decarboxylated products (see Scheme 2) were obtained with excellent (>95:5) diastereoselectivity, as measured by ^{1}H NMR spectroscopy, at 400 MHz, of the crude reaction mixtures, in favour of quenching from the axial direction.

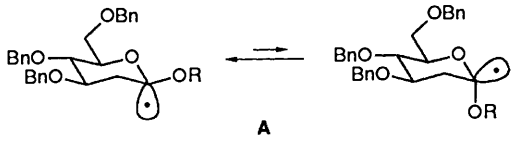


8–11

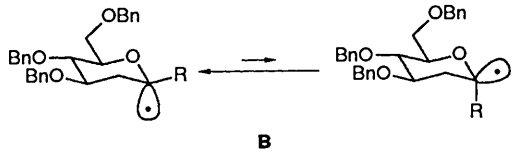
13 R = α/β-Me
14 R = $CH_2OCH_2CH_2SiMe_3$
15 R = $CH_2CH{=}CH_2$
16 R = CH_2Ph

Scheme 2 *Reagents and conditions:* i, Et_3N; ii, **12**; iii, R'SH, *hν* (W)

The anomeric configurations of the β-*C*-glycosides **13–16** were assigned unambiguously on the basis of the geminal and vicinal coupling constants associated with the axial and equatorial protons at C-2 in the ^{1}H NMR spectrum, owing to the complexity of the anomeric proton signal and its overlap with other signals. These same axial and equatorial proton signals, in an otherwise unobscured region of the spectrum, greatly facilitated the identification of the β-anomers as the sole products, within reasonable limits, of reductive decarboxylation.

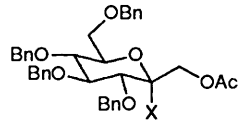


A

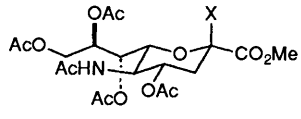


B

Comparison of the excellent selectivities observed here with those obtained in our earlier studies on the formation of 2-deoxy-*O*-glycosides under broadly similar conditions leads to the conclusion that radicals **B** are somewhat more face-selective than are radicals **A** in their reactions with thiols. The excellent selectivities observed for radicals **B** are entirely in accord with those observed by Vasella[10] for the related reaction of the nitro glycoside **17** with tributyltin hydride with exclusive formation of compound **18** and with the reported[15] reactions of the sialic ester chloride **19** with tributyltin hydride in which quenching took place selectively from the axial direction to give compound **20**. Similarly, *N*-bromosuccinimide-mediated radical bromination of various pyranoses and uronate and ulosonate esters occurs with highly selective quenching from the axial direction.[16] The increased selectivity observed in going from radicals **A** to **B** is best explained in terms, in each case, of pyramidalised σ-radicals[17] in the $^4C_1$ chair conformation with a greater bias for the axial disposition of the single electron in **B** than in **A** owing to the reduced preference of aliphatic carbon over oxygen substituents for the axial site at the anomeric position.[18]



17 X = NO_2
18 X = H



19 X = Cl
20 X = H

Experimental

General.—The general experimental details are as in Part 1.[7] *J*-values for NMR spectra are given in Hz.

Methyl 4,5,7-*Tri*-O-*benzyl*-2,3-*dideoxy*-2-*methyl*-α/β-D-arabino-*hept*-2-*ulopyranosonate* **3**.—*Method A.* A solution of the sulphone ester **1**[7] (200 mg, 0.32 mmol) in THF (10 cm^3) was stirred at −78 °C under nitrogen and treated with a solution of LN (lithium naphthalenide) in THF (1 mol dm^{-3}; 0.8 cm^3, 0.8 mmol) and subsequently with methyl iodide (0.04 cm^3, 0.65 mmol). After warming to room temperature the reaction mixture was poured into water and repeatedly extracted with diethyl ether. The combined extracts were washed successively with water and then brine, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the resultant oil on silica gel [eluent (40–60) light petroleum–diethyl ether (4:1)] gave the *title product* as an oil (80 mg, 50%) consisting of two unassigned anomers (3:5) with $[\alpha]_D^{20}$ +54° (*c* 1, $CHCl_3$); δ (400 MHz, major isomer) 1.46 (3 H, s), 1.52 (1 H, dd, $J_{3a,3e} = J_{3a,4}$ = 13.0, 3-H^a), 2.73 (1 H, dd, $J_{3a,3e}$ 13, $J_{3e,4}$ 4, 3-H^e), 3.52–3.57 (3 H, m, 4-, 5- and 6-H), 3.68 (3 H, s), 3.69–3.74 (2 H, m, 7-H_2), 4.48–4.86 (6 H, m, CH_2Ph) and 7.12–7.35 (15 H, m, Ph); δ (400 MHz, minor isomer) 1.44 (3 H, s), 1.49 (1 H, dd, $J_{3a,3e} = J_{3a,4}$ = 13.1, 3-H^a), 2.77 (1 H, dd, $J_{3a,3e}$ 13.1, $J_{3e,4}$ 4.7, 3-H^e), 3.45–3.49 (2 H, m, 7-H_2), 3.72 (3 H, s), 3.60–3.88 (3 H, m, 4-, 5- and 6-H), 4.62–4.94 (6 H, m, CH_2Ph) and 7.26–7.37 (15 H, m, Ph); $\nu_{max}(CHCl_3)/cm^{-1}$ 2865, 1742, 1495, 1451, 1361, 1284, 1194 and 1097; *m/z* 399 ($M^{\cdot+}$ − CH_2Ph), 293, 233 and 91 (Found: C, 73.4; H, 7.1. $C_{30}H_{34}O_6$ requires C, 73.45; H, 6.99%).

Methyl 4,5,7-*Tri*-O-*benzyl*-2,3-*dideoxy*-2-[(2-*trimethylsilylethoxy*)*methyl*]-β-D-arabino-*hept*-2-*ulopyranosonate* **4**.—The sulphone ester **1** (1.00 g, 1.62 mmol) was treated with LN and (2-trimethylsilylethoxy)methyl chloride (0.57 cm^3, 3.24 mmol) according to method A to give the *title compound* after chromatography on silica gel [eluent (40–60) light petroleum–diethyl ether (17:3)] in the form of an oil as a single anomer with $[\alpha]_D^{20}$ +38°; δ (400 MHz) −0.02 (9 H, s), 0.87–0.91 (2 H, m, CH_2SiMe_3), 1.57 (1 H, dd, $J_{3a,3e} = J_{3a,4}$ = 13, 3-H^a), 2.75 (1 H, dd, $J_{3a,3e}$ 13, $J_{3e,4}$ 4.4, 3-H^e), 3.52–3.64 (7 H, m, $CH_2OCH_2CH_2$-$SiMe_3$, 4-H, 5- and 6-H), 3.70 (3 H, s), 3.75–3.77 (2 H, m, 7-H_2), 4.52–4.87 (6 H, m, CH_2Ph) and 7.15–7.36 (15 H); $\nu_{max}(CHCl_3)/cm^{-1}$ 1735, 1500, 1450, 1250 and 1100; *m/z* 605 ($M^{\cdot+}$ − H), 548, 273, 181, 91 and 73 (Found: C, 69.2; H, 7.7. $C_{35}H_{46}O_7Si$ requires: C, 69.28; H, 7.64%).

Methyl 4,5,7-*Tri*-O-*benzyl*-2,3-*dideoxy*-2-(*prop*-2-*enyl*)-β-D-

arabino-*hept*-2-*ulopyranosonate* **5**.—*Method B.* LDA (1 mol dm^{-3}; 2.15 cm^3, 2.15 mmol) in THF was added to a stirred solution of the sulphone **2**[7] (1.00 g, 1.79 mmol) in THF (5 cm^5) at −78 °C under nitrogen. After the mixture had been stirred for 15 min at that temperature dimethyl carbonate (0.21 cm^3, 2.51 mmol) was added. When completion was indicated by TLC (SiO_2; light petroleum–diethyl ether, 4:1) a solution of LN (1 mol dm^{-3}; 4.48 cm^3, 4.48 mmol) was added followed by allyl bromide (0.3 cm^3, 3.58 mmol). The reaction mixture was then allowed to come to room to temperature before being poured into water and repeatedly extracted with diethyl ether. The extracts were washed sequentially with water and brine, then dried ($MgSO_4$), and concentrated under reduced pressure to give a viscous oil from which the title compound was isolated by chromatography on silica gel [eluent (40–60) light petroleum–diethyl ether (17:1)] as an oil (0.41 g, 44%) with $[\alpha]_D^{30}$ +42° (*c* 1.2, $CHCl_3$) (lit.,[7] $[\alpha]_D^{30}$ +42°) and spectral data in accord with those recorded in the literature.[7]

Methyl [2-*Benzyl*-4,5,7-*tri*-O-*benzyl*-2,3-*dideoxy*-β-D-arabino-*hept*-2-*ulopyranosonate* **6**.—The *title compound* was prepared from the sulphone **2** (1.00 g, 1.79 mmol), dimethyl carbonate (0.21 cm^3, 2.51 mmol) and benzyl bromide (0.43 cm^3, 3.58 mmol) by method **B**. After chromatography on silica gel [eluent (40–60) light petroleum–diethyl ether (17:1)] the *title compound* **6** was isolated as an oil (0.51 g, 56%) with $[\alpha]_D^{20}$ +34.4° 1, (*c* 1, $CHCl_3$); δ (400 MHz) 1.55 (1 H, dd, $J_{3a,3e}$ = $J_{3a,4}$ = 13, 3-H^a), 2.65 (1 H, dd, $J_{3a,3e}$ 13, $J_{3e,4}$ 4.1, 3-H^e), 2.99–3.08 (2 H, m, CCH_2Ph), 3.59 (3 H, s), 3.51–3.79 (5 H, m, 4-H, 5- and 6-H and 7-H_2), 4.54–4.87 (6 H, m, OCH_2Ph) and 7.16–7.38 (20 H, Ph); $\nu_{max}(CHCl_3)/cm^{-1}$ 1735, 1500, 1450, 1380 and 1100; *m/z* 566 ($M^{\bullet+}$), 475, 369, 351, 309, 261, 181 and 91 (Found: C, 76.4; H, 6.7. $C_{36}H_{38}O_6$ requires C, 76.30; H, 6.76%).

3,4,6-*Tri*-O-*benzyl*-1,2-*dideoxy*-1β-*methyl*-D-arabino-*hexopyranose** **13**. *General Method for Saponification and Reductive Decarboxylation.*—A solution of the ester **3** (250 mg, 0.51 mmol) in MeOH (0.5 cm^3)–THF (1 cm^3) was treated at room temperature with a solution of potassium hydroxide (69 mg) in water (0.2 cm^3) and the reaction mixture was stirred until TLC indicated complete reaction. The reaction mixture was then diluted with methylene dichloride (10–20 cm^3), washed with 2 mol dm^{-3} hydrochloric acid, dried ($MgSO_4$), and concentrated under reduced pressure to give the crude acid **8** (210 mg, 88%).

Without further purification, this acid (186 mg, 0.39 mmol) was taken up in methylene dichloride (3 cm^3) and the solution was stirred in the dark under argon at room temperature with triethylamine (0.07 cm^3, 0.49 mmol) and the salt **12** (93 mg, 0.49 mmol). After 1 h, t-dodecanethiol (0.46 cm^3, 0.2 mmol) was added to the yellow solution and the reaction mixture was cooled to 0 °C and photolysed with a 500 W tungsten lamp for 1 h. Evaporation of the volatiles under reduced pressure and chromatography of the residue on silica gel [eluent (40–60) light petroleum–diethyl ether (85:15)] gave the *title product*, a single anomer, as an oil (94 mg, 56%) with $[\alpha]_D^{20}$ +23° (*c* 1, CCl_4); δ (400 MHz) 1.26 (3 H, d, *J* 6.14, Me), 1.44 (1 H, ddd, $J_{2a,2e}$ = $J_{2a,3}$ = $J_{1,2a}$ = 11.5, 2-H^a), 2.13 (1 H, ddd, $J_{2a,2e}$ 11.5, $J_{2e,3}$ 1.8, $J_{1,2e}$ 3.2, 2-H^e), 3.42 (1 H, ddd, $J_{4,5}$ 12.6, $J_{5,6a}$ 4.8, $J_{5,6b}$ 1.9, 5-H), 3.47 (1 H, dd, $J_{3,4}$ = $J_{4,5}$ = 12.6, 4-H), 3.51 (1 H, m, 1-H), 3.61–3.74 (3 H, m, 3-H and 6-H_2), 4.50–4.89 (6 H, m, CH_2Ph) and 7.15–7.36 (15 H, Ph); $\nu_{max}(CHCl_3)/cm^{-1}$ 1500, 1450, 1365 and 1100; *m/z* 417 ($M^{\bullet+}$ − Me), 181, 169, 145, 127, 105, 97, 91 and 77 (Found: C, 77.5; H, 7.6. $C_{28}H_{32}O_4$ requires C, 77.75; H, 7.46%).

3,4,6-*Tri*-O-*benzyl*-1,2-*dideoxy*-1β-(2-*trimethylsilylethoxy*)-*methyl*]-D-arabino-*hexopyranose** **14**.—Saponification of the ester **4** (200 mg) according to the standard protocol gave the acid **9** (160 mg, 82%). This acid (150 mg) was decarboxylated according to the standard method to give, after chromatography on silica gel [eluent (40–60) light petroleum–diethyl ether (4:1)], the *title compound* as an oil in the form of a single anomer (80 mg, 58%) with $[\alpha]_D^{20}$ +15° (*c* 1, $CHCl_3$); δ (400 MHz) 0.02 (9 H, s), 0.94 (2 H, m, CH_2SiMe$_3$), 1.43 (1 H, ddd, $J_{2a,2e}$ = $J_{2a,3}$ = $J_{1,2a}$ = 11.2, 2-H^a), 2.24 (1 H, ddd, $J_{2a,2e}$ 11.2, $J_{2e,3}$ 1.1, $J_{1,2e}$ 5, 2-H^e), 3.34–3.82 (9 H, m, 3-H, 4- and 5-H, 6-H_2, and CH_2OCH_2CH$_2$SiMe$_3$), 4.50–4.96 (6 H, m, CH_2Ph) and 7.15–7.34 (15 H, Ph); $\nu_{max}(CHCl_3)/cm^{-1}$ 2865, 1601, 1528, 1495, 1451, 1361 and 1091; *m/z* 457 ($M^{\bullet+}$ − CH_2Ph), 447, 215, 181 and 91 (Found: C, 72.0; H, 8.0. $C_{33}H_{44}O_5Si$ requires C, 72.22; H, 8.08%).

3,4,6-*Tri*-O-*benzyl*-1,2-*dideoxy*-1β-(*prop*-2-*enyl*)-D-arabino-*hexopyranose** **15**.—Saponification of the ester **5** (260 mg) according to the standard protocol gave the acid **10** (200 mg, 77%), which was immediately subjected to the standard decarboxylation procedure to give, after chromatography on silica gel [eluent (40–60) light petroleum–diethyl ether (19:1)], the *title product*, a single anomer, as an oil (130 mg, 73%) with $[\alpha]_D^{20}$ +7.6° (*c* 1, $CHCl_3$); δ (400 MHz) 1.39 (1 H, ddd, $J_{2a,3}$ = $J_{2a,2e}$ = $J_{1,2a}$ = 11.8, 2-H^a), 2.18 (1 H, ddd, $J_{2a,2e}$ 11.8, $J_{2a,3}$ 1.8, $J_{1,2e}$ 3.2, 2-H^e), 2.22–2.46 (2 H, m, CH_2CH=CH$_2$), 3.39 (1 H, m, 5-H), 3.41 (1 H, ddd, $J_{2a,3}$ 11.8, $J_{2e,3}$ 1.8, $J_{3,4}$ 8.6, 3-H), 3.48 (1 H, dd, $J_{3,4}$ = $J_{4,5}$ 8.6, 4-H), 3.63 (1 H, m, 1-H), 3.70 (2 H, m, 6-H), 4.52–5.08 (6 H, m, CH_2Ph), 5.11 (2 H, m, CH$_2$CH=CH_2), 5.83 (1 H, m, CH$_2$CH=CH$_2$) and 7.17–7.37 (15 H, Ph); $\nu_{max}(CHCl_3)/cm^{-1}$ 3049, 1500, 1450, 1370 and 1100; *m/z* 368 ($M^{\bullet+}$ + H − CH_2Ph), 181, 153, 107, 91 and 41 (Found: C, 78.4; H, 7.4. $C_{30}H_{34}O_4$ requires C, 78.57; H, 7.47%).

1β-*Benzyl*-3,4,6-*tri*-O-*benzyl*-1,2-*dideoxy*-D-arabino-*hexopyranose** **16**.—Saponification of the ester **6** (200 mg) according to the standard method gave the acid **11** (72%). This acid (130 mg) was subjected to the standard decarboxylation procedure to give, after chromatography on silica gel [eluent (40–60) light petroleum–diethyl ether (9:1)], the *title product*, a single anomer, as a crystalline solid (110 mg, 92%) with m.p. 42–43 °C [from (40–60) diethyl ether–light petroleum]; $[\alpha]_D^{20}$ +8° (*c* 1, $CHCl_3$); δ (400 MHz) 1.45 (1 H, ddd, $J_{2a,3}$ = $J_{2a,2e}$ = $J_{1,2a}$ = 12.6, 2-H^a), 2.13 (1 H, ddd, $J_{2a,2e}$ 12.6, $J_{2e,3}$ 1.6, $J_{1,2e}$ 4.9, 2-H^e), 2.9 (2 H, m, CCH_2Ph), 3.42 (1 H, ddd, $J_{4,5}$ 9.6, $J_{5,6a}$ 4.6, $J_{5,6b}$ 1.9, 5-H), 3.51 (1 H, dd, $J_{3,4}$ = $J_{4,5}$ = 9.6, 4-H), 3.57–3.63 (2 H, m, 1- and 3-H), 3.69–3.78 (2 H, m, 6-H_2), 4.55–4.91 (6 H, m, CH_2Ph) and 7.19–7.38 (20 H, Ph); $\nu_{max}(CHCl_3)/cm^{-1}$ 1500, 1450 and 1085; *m/z* 507 ($M^{\bullet+}$ − H), 417, 293, 203, 181 and 91 (Found: C, 80.1; H, 7.3. $C_{34}H_{36}O_4$ requires C, 80.28; H, 7.13%).

Acknowledgements

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References

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* *Systematic names*: **13**, 2,6-*anhydro*-4,5,7-*tri*-O-*benzyl*-1,3-*dideoxy*-D-gluco-*heptitol*; **14**, 2,6-*anhydro*-4,5,7-*tri*-O-*benzyl*-3-*deoxy*-1-O-[2-(trimethylsilyl)ethyl]-D-gluco-*heptitol*; **15**, 4,8-*anhydro*-6,7,9-*tri*-O-*benzyl*-1,2,3,5-*tetradeoxy*-D-gluco-*non*-1-*enitol*; **16**, 2,6-*anhydro*-4,5,7-*tri*-O-*benzyl*-1,3-*dideoxy*-1-*phenyl*-D-gluco-*heptitol*.

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