77. Deoxy-nitrosugars

4th Communication[1]

Convenient Synthesis of 1-Deoxy-1-nitroaldoses

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Summary

A new synthesis of 1-deoxy-1-nitroaldoses by ozonolysis of *N*-glycosylnitrones according to the procedure of *Bailey et al.* is described. Based on the oxime **1**, the mannofuranosylnitrones **3–5** were obtained in yields of 86–88% and the 1-deoxy-1-nitromannose **6** in yields of 70–76%. In the same manner the 1-deoxy-1-nitroaldoses **9**, **12**, **18**, and **19** were prepared in yields of 61–90% from the oximes **7**, **10**, **14** and **15**, the procedure being compatible with the presence of free hydroxy groups.

1-Deoxy-1-nitroaldoses are useful intermediates for the synthesis of chain elongated sugars [1]. They have been prepared in fair yields from aldose-oximes *via* aldonolactone oximes, 1-*C*-nitroso-glycosylhalides and 1-*C*-nitro-glycosylhalides [2]. This method is however incompatible with the presence of a free C(2)–OH group[3]).

We now report a shorter route to 1-deoxy-1-nitroaldoses, which proceeds in high yields and which is compatible with the presence of a free C(2)–OH group. It is based on the ozonolysis of *N*-glycosylnitrones to nitrocompounds according to *Bailey et al.* [3].

N-Glycosylnitrones have not been isolated previously but they have been formed *in situ* from sugar oximes and aliphatic aldehydes and used for the diastereoselective cycloaddition to olefines [4–5]. Since *C*-arylnitrones are easily formed and isolated [6] [7] we investigated the preparation of the nitrones **3–5** from 2,3:5,6-di-*O*-isopropylidene-D-mannose oxime (**1**) (*via* the tautomeric *N*-glycosylhydroxylamine **2**) [4b] and 4-methoxy-, 4-chloro- and 4-nitrobenzaldehyde,

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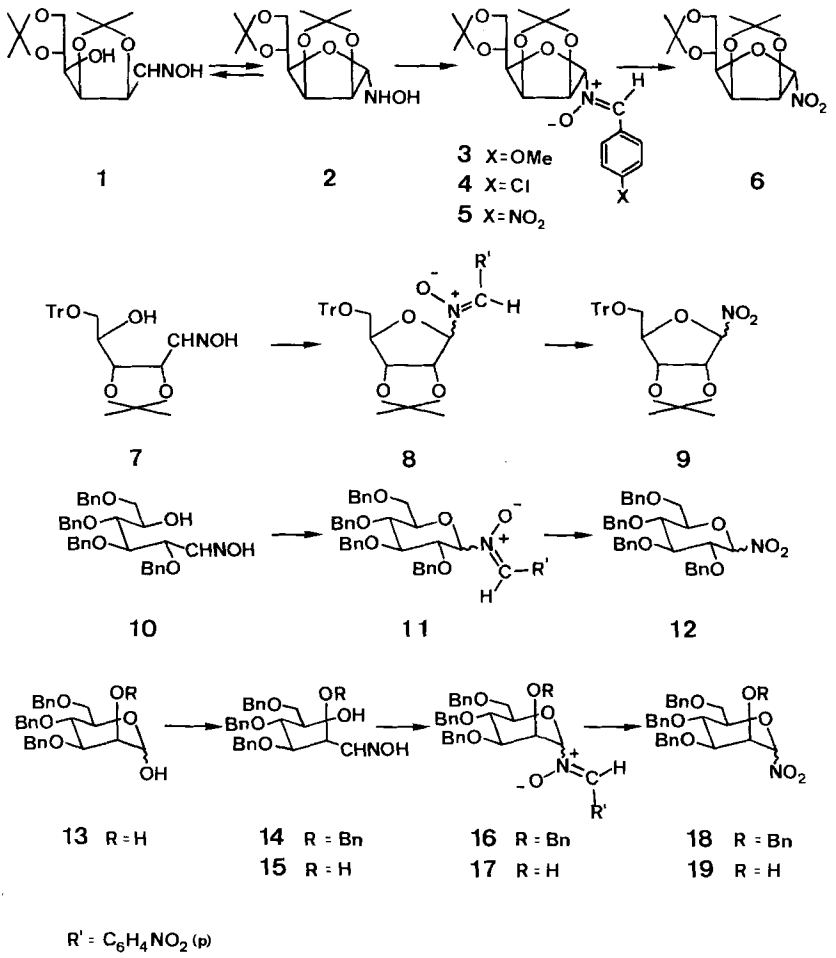
[3]) The first step in this sequence (oxidation of aldose oximes with periodate) failed in the case of 3,4,6-tri-*O*-benzyl-D-mannoseoxime.

Scheme



respectively. In each case crystalline nitrones (**3–5**) were isolated in yields of 86–88%[4]) (see *Scheme*).

These nitrones were stable enough to be sublimed in high vacuum without decomposing. Their oxidation with ozone (CH_2Cl_2, $-78°$) gave in each case the 1-deoxy-1-nitromannose (**6**) in yields of 70–76% (see *Table*). The standard procedure involves boiling the aldose oxime with a small excess of 4-nitrobenzaldehyde overnight in CH_2Cl_2, then cooling the solution to $-78°$ and treating with ozone until disappearance of the starting nitrone.

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[4]) In the ^{1}H-NMR. spectrum of each of the nitrones **3–5**, H–C(1) appears as a singulet confirming the α-D-configuration. The (*Z*)-configuration of the nitrones is assumed on the base of the higher stability of (*Z*)-aldonitrones [6] [8].

Table. *Yields of 1-deoxy-1-nitroaldoses*

Starting material	Aldehyde used for the formation of the nitrones	Product	Overall Yield
1	(*p*)-$CH_3O-C_6H_4-CHO$	**6**	70%
1	(*p*)-$Cl-C_6H_4-CHO$	**6**	76%
1	(*p*)-$O_2N-C_6H_4-CHO$	**6**	70%
7	(*p*)-$O_2N-C_6H_4-CHO$	**9**	90%
10	(*p*)-$O_2N-C_6H_4-CHO$	**12**	73%
14	(*p*)-$O_2N-C_6H_4-CHO$	**18**	68%
13	(*p*)-$O_2N-C_6H_4-CHO$	**19**	61%

This procedure was applied to the 2,3-*O*-isopropylidene-5-*O*-trityl-D-ribose oximes (**7**) [4a], giving a mixture of two nitrones **8**[5]) which gave after oxidation 90% of the 1-deoxy-1-nitroribose (**9**) indicating the compatibility of the trityl group with this procedure.

The tetrabenzylglucose oxime **10** [9] also gave a mixture of two nitrones **11**[6]). A partial over-oxidation took place during ozonolysis which led to by-product(s) (benzoates?) which were difficult to separate from **12** by chromatography[7]) and showed an IR. absorption at 1725 cm^{-1}. Treatment of the crude product (obtained after extraction of the 4-nitrobenzaldehyde) with $LiBH_4$ (s. *Exper. Part*) transformed the by-product(s) into a more polar material allowing an easy purification of the known [2] [9] 1-deoxy-1-nitroglucose **12** (mixture of anomers; 73% yield).

Over-oxidation was not observed during the preparation of 2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-nitro-D-mannopyranose (**18**) [2], which was obtained from the nitrones **16** (see *Exper. Part*) as a mixture of anomers in a yield of 68%.

To check the compatibility of this procedure with the presence of a C(2)–OH group, the crude oxime **15**, obtained from 3,4,6-tri-*O*-benzyl-D-mannose (**13**) [10] (see *Exper. Part*) was treated with 4-nitrobenzaldehyde forming the nitrones **17** which were immediately ozonized. Purification by treatment with $LiBH_4$ and chromatography gave the 3,4,6-tri-*O*-benzyl-1-deoxy-1-nitro-D-mannopyranose (**19**) as a mixture of anomers in an overall yield of 61%.

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Experimental Part

General Remarks. See [9]. The aldehydes used were obtained from *Fluka (purum)*.

Preparation of N-*(4-methoxybenzylidene)-2,3:5,6-di*-O-*isopropylidene-a*-D-*mannofuranosylamine* N-*oxide* (**3**). A solution of 550 mg (2 mmol) of **1** and 408 mg (3 mmol) of anisaldehyde in 5 ml $CHCl_3$ was heated under reflux for 54 h. The solvent was evaporated and the excess of anisaldehyde removed in HV. Recrystallisation (CH_2Cl_2/hexane) of the crude product (831 mg, m.p. < 150°) gave 440 mg

[5]) The nitrones were not isolated. They appeared as two yellow spots on TLC. (AcOEt/hexane 1:2, Rf 0.31 and 0.25).

[6]) Two yellow spots on TLC. (AcOEt/toluene 1:9, Rf 0.33 and 0.23).

[7]) TLC. (dimethoxyethane/hexane 1:3): small spot with Rf 0.50, besides **12** (Rf 0.58).

(56%) of **3** (m.p. 170–170.5°). Recrystallization of the residue of the mother liquors gave an additional 246 mg (31%) of **3**. An analytical sample was obtained by sublimation (140°/0.001 Torr), m.p. 170–170.5°, $[\alpha]_D = +68.5°$ ($c = 1.1$ Lsgm.). – IR.: 3100 *S*, 3070 *S*, 2990*s*, 2940*m*, 2900 *S*, 2840*w*, 2450*w* br., 1604*s*, 1568*w*, 1508*s*, 1464 *S*, 1458*m*, 1444*m*, 1423*w*, 1403*w*, 1388*s*, 1378*s*, 1348*w*, 1324*m*, 1309*m*, 1174*s*, 1145*s*, 1119*s*, 1098*s*, 1072*s*, 1034*s*, 993 *S*, 983*w*, 970*w*, 948*m*, 890*m*, 845*s*. – ^{1}H-NMR.: 8.34–8.13 (*m*, 2 arom. H); 7.48 (*s*, H–C=N); 7.01–6.84 (*m*, 2 arom. H); 5.45 (*s*, H–C(1)); 5.35 (*d*, $J = 6.0$, H–C(2)); 5.02 (*d*×*d*, $J = 6.0$ and 3.7, H–C(3)); 4.72 (*d*×*d*, $J = 6.9$ and 3.7, H–C(4)); 4.38 (*d*×*t*, $J = 6.9$ and 5.4, H–C(5)); 4.12 (*d*, $J = 5.4$, 2 H–C(6)); 3.86 (*s*, CH_3O); 1.53 (*s*, H_3C); 1.47 (*s*, H_3C); 1.38 (*s*, 2 H_3C). – ^{13}C-NMR.: 161.40 (*s*), 132.94 (*d*), 130.86 (*d*), 122.32 (*s*), 113.80 (*d*), 112.95 (*s*), 109.11 (*s*), 102.95 (*d*), 85.49 (*d*), 84.39 (*d*), 80.30 (*d*), 73.20 (*d*), 66.47 (*t*), 55.26 (*qa*), 26.74 (*qa*), 25.95 (*qa*), 25.16 (*qa*), 24.36 (*qa*). – MS. (70 eV): 393 (6), 378 (6), 376 (17), 185 (48), 135 (13), 134 (18), 127 (39), 121 (14), 103 (12), 101 (34), 99 (28), 85 (31), 77 (12), 71 (21), 69 (30), 59 (36), 57 (17), 55 (14), 44 (22), 43 (100), 41 (34), 38 (16).

$C_{20}H_{27}NO_7$ (393.44) Calc. C 61.06 H 6.92 N 3.56% Found C 61.06 H 6.84 N 3.51%

Preparation of N-*(4-chlorobenzylidene)-2,3:5,6-di*-O-*isopropylidene-α*-D-*mannofuranosylamine* N-*oxide* (**4**). A solution of 550 mg (2 mmol) of **1** and 421 mg (3 mmol) of 4-chlorobenzaldehyde in 5 ml CH_2Cl_2 was heated under reflux for 16 h. The solvent was evaporated and the excess of 4-chlorobenzaldehyd was removed by sublimation (r.t./0.01 Torr). Recrystallization (CH_2Cl_2/hexane) of the crude product (825 mg, m.p. 160–165°) gave 684 mg (86%) of **4**, m.p. 166–166.5°. Sublimation (130°, 0.001 Torr) afforded an analytical sample, m.p. 166.5–167°, $[\alpha]_D = +51.6°$ ($c = 1.2$, Lsgm.). – IR.: 3080 *S* br., 2990*s*, 2940*m*, 2890*w*, 2450*w* br., 1592*m*, 1557*w*, 1488*m*, 1457*m*, 1413*m*, 1406*m*, 1388*s*, 1379*s*, 1347*m*, 1314*m*, 1151*s*, 1122*s*, 1094*s*, 1072*s*, 1016*s*, 992 *S*, 982*w*, 971*m*, 948*m*, 892*m*, 862 *S*, 846*s*. – ^{1}H-NMR.: 8.32–8.08 (*m*, 2 arom. H); 7.56 (*s*, H–C=N); 7.50–7.33 (*m*, 2 arom. H); 5.47 (*s*, H–C(1)); 5.33 (*d*, $J = 6.0$, H–C(2)); 4.98 (*d*×*d*, $J = 6.0$ and 3.6, H–C(3)); 4.67 (*d*×*d*, $J = 6.6$ and 3.6, H–C(4)); 4.41 (*d*×*t*, $J = 6.6$ and 5.4, H–C(5)); 4.12 (*d*, $J = 5.4$, 2 H–C(6)); 1.53 (*s*, H_3C); 1.47 (*s*, H_3C); 1.38 (*s*, 2 CH_3). – ^{13}C-NMR.: 136.41 (*s*), 131.90 (*d*), 129.96 (*d*), 128.68 (*d*), 127.82 (*s*), 113.16 (*s*), 109.14 (*s*), 103.30 (*d*), 85.47 (*d*), 84.41 (*d*), 80.16 (*d*), 73.13 (*d*), 66.37 (*t*), 26.75 (*qa*), 25.96 (*qa*), 25.13 (*qa*), 24.38 (*qa*). – MS. (70 eV): 397 (2), 382 (7), 185 (84), 127 (38), 103 (10), 101 (34), 99 (28), 97 (11), 85 (29), 81 (10), 73 (10), 71 (19), 69 (26), 59 (34), 57 (14), 43 (100), 41 (27), 39 (11).

$C_{19}H_{24}ClNO_6$ (397.86) Calc. C 57.36 H 6.08 N 3.52% Found C 57.35 H 6.03 N 3.38%

Preparation of N-*(4-nitrobenzylidene)-2,3:5,6-di*-O-*isopropylidene-α*-D-*mannofuranosylamine* N-*oxide* (**5**). A solution of 550 mg (2 mmol) of **1** and 302 mg (2 mmol) of 4-nitrobenzaldehyde in 5 ml CH_2Cl_2 was stirred at r.t. for 30 h. The solution was concentrated. Addition of hexane gave 802 mg (98%) of **5** (m.p. 138–141°). Recrystallization (CH_2Cl_2/hexane) gave 605 mg (74%) of **2**, m.p. 140.5–142.5°. Chromatography (20 g SiO_2, AcOEt/hexane 1:3) of the residue of the mother liquors and recrystallization gave 113 mg (14%) of **5**. An analytical sample was obtained by sublimation (130°/0.001 Torr), m.p. 142–142.5°, $[\alpha]_D + 41.7°$ ($c = 1.0$, Lsgm.). – UV. (CH_2Cl_2): 347 (17100), 249 (9200). – IR.: 3110*w*, 3070*w*, 2995*s*, 2940*m*, 2890*w*, 2450*w*, 1600*m*, 1564*m*, 1520*s*, 1490*w*, 1457*m*, 1419*w*, 1388*s*, 1378*s*, 1345*s*, 1318*m*, 1153*s*, 1115 *S*, 1102*s*, 1070*s*, 1015*w*, 992 *S*, 982*w*, 969*m*, 949*m*, 865*s*. – ^{1}H-NMR.: 8.50–8.13 (*m*, 4 arom. H); 7.73 (*s*, H–C=N); 5.50 (*s*, H–C(1)); 5.32 (*d*, $J = 5.7$, H–C(2)); 4.97 (*d*×*d*, $J = 5.7$ and 3.6, H–C(3)); 4.63 (*d*×*d*, $J = 6.6$ and 3.6, H–C(4)); 4.42 (*d*×*t*, $J = 6.6$ and 5.1, H–C(5)); 4.13 (*d*, $J = 5.1$, 2 H–C(6)); 1.53 (*s*, CH_3); 1.47 (*s*, CH_3); 1.38 (*s*, 2 CH_3). – ^{13}C-NMR.: 147.96 (*s*), 134.91 (*s*), 130.56 (*d*), 129.08 (*d*), 123.66 (*d*), 113.40 (*s*), 109.20 (*s*), 103.83 (*d*), 85.50 (*d*), 84.48 (*d*), 80.03 (*d*), 73.08 (*d*), 66.28 (*t*), 26.77 (*qa*), 25.99 (*qa*), 25.08 (*qa*), 24.41 (*qa*). – MS. (70 eV): 393 (4), 243 (5), 185 (57), 127 (27), 103 (9), 101 (27), 99 (21), 97 (9), 85 (24), 81 (9), 73 (10), 71 (17), 69 (24), 59 (30), 57 (14), 55 (10), 49 (9), 44 (11), 43 (100), 42 (8), 41 (31), 39 (14).

$C_{19}H_{24}N_2O_8$ (408.41) Calc. C 55.88 H 5.92 N 6.86% Found C 55.94 H 5.87 N 6.72%

Preparation of N-*(4-nitrobenzylidene)-2,3,4,6-tetra*-O-*benzyl*-D-*mannofuranosylamine* N-*oxide* (**16**). A solution of 556 mg (1 mmol) of **14** [9] and 181 mg (1.2 mmol) of 4-nitrobenzaldehyde in 5 ml of CH_2Cl_2 was boiled under reflux for 14 h. After concentration of the solution the two yellow nitrones (Rf 0.30 and 0.20, AcOEt/toluene 1:9) were separated by flash-chromatography [11] (silica gel, 350 ml AcOEt/toluene 5:95, then 10:90). The nitrone with Rf 0,30 (266 mg, 39%) was isolated (yellow oil). $[\alpha]_D = +48,9°$ ($c = 1,3$). – IR.: 3090 *S*, 3070*w*, 3010*m*, 2920*w*, 2870*m*, 1600*m*, 1560*w*, 1520*s*, 1497*m*, 1455*m*, 1420*w*, 1345*s*, 1325 *S*, 1110*s* br., 1030*m*, 940*w*, 912*w*, 865*m*. – ^{1}H-NMR.: 8.31 and 8.17

(*AB*-system, $J=9$, $C_6H_4NO_2$); 7.83 (*s*, H–C=N); 7.43–7.05 (*m*, 4 C_6H_5); 5.46 (*d*, $J=4.4$, H–C(1)); 4.83 (*d*×*d*, $J=4.4$ and 2.1, H–C(2)); 4.77–4.28 (*m*, 4 CH_2–Ph); 4.28–3.64 (*m*, 5 H). – ^{13}C-NMR.: 147.67 (*s*), 137.76 (2*s*), 137.50 (*s*), 137.41 (*s*), 135.26 (*s*), 130.90 (*d*), 128.97 (*d*), 128.20 (*d*), 127.81 (*d*), 127.66 (*d*), 123.51 (*d*), 95.61 (*d*), 77.39 (*d*), 75.99 (*d*), 74.21 (*d*), 73.46 (*t*), 73.24 (*d*+2 *t*), 72.17 (*t*), 69.18 (*t*).

$C_{41}H_{40}N_2O_8$ (688.78) Calc. C 71.50 H 5.85 N 4.07% Found C 71.41 H 5.86 N 4.02%

A second fraction gave 374 mg (54%) of the nitrone with Rf 0.20 (yellow oil), $[\alpha]_D = +63.9°$ ($c=1.3$). – IR.: 3090*w*, 3070*w*, 3010*m*, 2920*w*, 2870*m*, 1600*m*, 1575*m*, 1519*s*, 1496*m*, 1455*m*, 1425*m*, 1360*m*, 1345*s*, 1307*m*, 1170*m*, 1110*s* br., 1040*m*, 1029*m*, 1000 *S*, 914*w*, 866*m*. – ^{1}H-NMR.: 8.35 and 8.20 (*AB*-system, $J=9$, $C_6H_4NO_2$); 7.90 (*s*, H–C=N); 7.45–7.00 (*m*, 4 C_6H_5); 4.94 (*s*, H–C(1)); 4.93 (*d*, $J=11.1$, 1 H); 4.85–4.57 (*m*, 7 H); 4.45 (*d*, $J=11.1$, 1 H); 4.15–3.52 (*m*, 5 H). – ^{13}C-NMR.: 147.68 (*s*), 137.66 (3*s*), 137.45 (*s*), 135.16 (*s*), 131.00 (*d*), 129.41 (*d*), 128.20 (*d*), 127.82 (*d*), 127.74 (*d*), 127.48 (*d*), 123.40 (*d*), 94.77 (*d*), 82.39 (*d*), 77.97 (*d*), 75.20 (2*t*), 74.00 (*d*), 73.78 (*d*), 73.22 (*t*), 71.98 (*t*), 68.78 (*t*).

$C_{41}H_{40}N_2O_8$ (688.78) Calc. C 71.50 H 5.85 N 4.07% Found C 71.60 H 5.83 N 4.09%

*Typical procedure for the synthesis of 1-deoxy-1-nitro-aldoses from aldoses (synthesis of 3,4,6-tri-O-benzyl-1-deoxy-1-nitro-*D*-manno-pyranose;* **19**). To a stirred solution of 69 mg (3 mmol) Na in 10 ml 96% aqueous ethanol were added at 60° 280 mg (4 mmol) of hydroxylamine hydrochloride. Stirring was continued for 5 min (pH 7) and 901 mg (2 mmol) of 3,4,6-tri-*O*-benzyl-D-mannose [10] was added. After 4½ h at 60° the reaction mixture was diluted with AcOEt, washed with sat. NaCl-solution and dried ($MgSO_4$). The solvent was removed under reduced pressure. The solution of the crude oxime and 453 mg (3 mmol) of *p*-nitrobenzaldehyde in 10 ml CH_2Cl_2 was heated under reflux for 14 h. TLC. (AcOEt/toluene 1:3) showed only a slight spot of the oxime (Rf 0.07) and a new yellow spot (Rf 0.33). The solution was diluted to 20 ml with CH_2Cl_2 and ozonolyzed at −78° (yellow → green → blue). TLC. (AcOEt/toluene 1:3) showed two new spots (Rf 0.51 and 0.46) besides *p*-Nitrobenzaldehyde (Rf 0.57). After adding 220 µl of dimethyl sulfide the reaction mixture was allowed to warm to r.t. *p*-Nitrobenzaldehyde was extracted 3× with a 10% aqueous solution of $NaHSO_3$[8]), the organic layer washed with sat. NaCl-sol. and dried ($MgSO_4$). After concentration under reduce pressure and flash chromatography (90 g SiO_2, AcOEt/hexane 1:3), 669 mg (70%) of **19** containing a small impurity (IR. absorption at 1725 cm^{-1})[9]) were isolated as an oil. A solution of this oil in 4 ml diglyme was added to a suspension of 30 mg (0.7 mmol) LiCl and 26 mg (0.7 mmol) $NaBH_4$ in 1.5 ml diglyme. After 40 min the solution was neutralized with 160 µl of acetic acid. After addition of AcOEt the solution was extracted with 10% aqueous $NaHCO_3$-solution, washed with sat. NaCl-solution and dried ($MgSO_4$). After concentration under reduce pressure, flash chromatography (30 g SiO_2, AcOEt/hexane 1:3) yielded 588 mg (61%) of **19** as a mixture of 77% of *α*-D-**19** and 23% *β*-D-**19**, $[\alpha]_D = +52.5°$ ($c=1.3$). – IR.: 3570*w*, 3090*w*, 3060*w*, 3000*m*, 2920*m* br., 2870*m*, 1575*s*, 1560*s*, 1495*w*, 1453*m*, 1360*s*, 1320*m* br., 1173*m*, 1100*s*, 1060 *S*, 1026*s*, 100 *S*, 910*w*, 895 *S*, 880 *S*. – MS. (70 eV): 388 (3), 105 (11), 91 (100), 77 (22), 59 (18), 45 (15).

$C_{27}H_{29}NO_7$ (479.53) Calc. C 67.63 H 6.10 N 2.92% Found C 67.88 H 6.21 N 3.19%

The first fractions of a flash chromatography (SiO_2 AcOEt/toluene 1:3) contained a higher proportion of *β*-D-**19** (Rf 0.51) and the last ones gave almost pure *α*-D-**19** (Rf 0.46). Two fractions were used for NMR. spectroscopic analysis.

First fraction (28% *α*-D-**19**: 72% *β*-D-**19**): $[\alpha]_D = +29.9°$ ($c=1.1$). – ^{1}H-NMR.: 7.52–6.97 (*m*, 3 C_6H_5); 5.62 (*d*, $J=2.5$, 0.28 H–C(1)); 5.17 (*d*, $J=1.5$, 0.72 H–C(1′)); 4.92–3.38 (*m*, 12 H); 2.65 (br., HO). – ^{13}C-NMR.: 137.66 (*s*), 137.53 (*s*), 136.87 (*s*), 128.51 (*d*), 128.26 (*d*), 128.09 (*d*), 127.86 (*d*), 127.78 (*d*), 127.72 (*d*), 127.59 (*d*), 101.68 (*d*), 80.91 (*d*), 77.62 (*d*), 75.17 (*t*), 73.49 (*t*), 73.02 (*d*), 72.00 (*t*), 68.13 (*t*), 67.90 (*d*) together with signals of lower intensity from *α*-D-**19**.

Second fraction (93% *α*-D-**19**: 7% *β*-D-**19**): $[\alpha]_D + 60.4°$ ($c=1.6$). – ^{1}H-NMR.: 7.45–7.03 (*m*, 3 C_6H_5); 5.63 (*d*, $J=2.5$, 0.93 H–C(1)); 5.20 (*d*, $J=1.5$, 0.07 H–C(1′)); 4.85–4.37 (*m*, 7 H); 4.28–3.87 (*m*, 2 H);

[8]) After addition of 15 g Na_2CO_3 to the combined $NaHSO_3$ extracts (150 ml), saturation with NaCl, extraction with CH_2Cl_2 and drying ($MgSO_4$), 366 mg (80% of the starting *p*-nitrobenzaldehyde) were recuperated.

[9]) An analogous impurity was also found in the synthesis of **12** and removed by the same treatment. In the other cases pure products were obtained without treatment with $NaBH_4$/LiCl.

3.75 (*d*, $J = 2.7$, 2 H–C(6)); 3.63 (*d* × *d*, $J = 7.5$ and 3.0, H–C(3)); 2.63 (br., HO). – ^{13}C-NMR.: 137.60 (*s*), 136.96 (*s*), 128.53 (*d*), 128.27 (*d*), 128.15 (*d*), 127.83 (*d*), 127.75 (*d*), 127.64 (*d*), 105.12 (*d*), 78.29 (*d*), 76.55 (*d*), 74.80 (*t*), 73.42 (*t*), 72.60 (*d*), 72.52 (*t*), 68.16 (*t*), 67.90 (*d*).

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