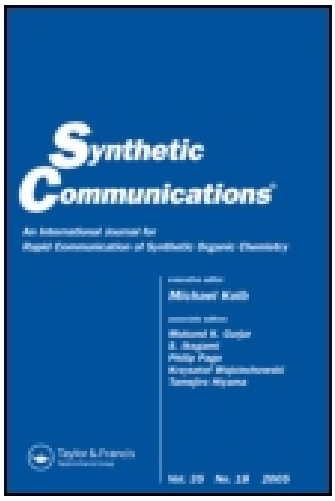

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A Convenient Synthesis of Pyranosyl-1-carbaldoximes

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ABSTRACT

A simple high-yielding procedure is described for the preparation of tri-*O*-acetyl-β-L-fucopyranosylformaldoxime (**1**) involving stannate(II)-mediated reduction of the readily accessible tri-*O*-acetyl-β-L-fucopyranosylnitromethane (**3**). The D-mannosyl, D-glucosyl, D-galactosyl, and D-xylosyl analogues **7–12** were prepared similarly. The structure of tetra-*O*-acetyl-β-D-mannopyranosylformaldoxime (**7**) was determined by X-ray crystallography.

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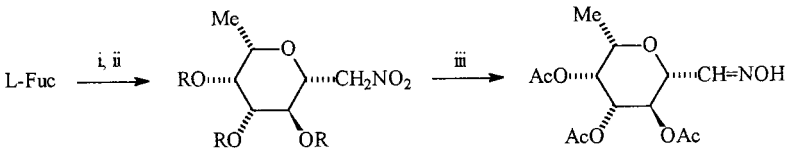
Key Words: *C*-Glycosides; Pyranosylcarbaldoximes; Pyranosylnitromethanes; X-Ray crystallography.

INTRODUCTION

While investigating new synthetic approaches to *C*-glycosides[1] we required a simple method for the preparation of pyranose-1-carbaldoximes (2,6-anhydro-1-deoxy-1-hydroxyimino-heptitols). The recent article by Phan-Huu et al.[2] describing a route to such compounds therefore prompts us to report the method we have been using. We initially considered a traditional approach via oximation of *C*-pyranosyl aldehydes. However, literature routes[3–5] to the aldehydes all involve several stages, some of which require expensive reagents and/or forcing conditions, and the aldehydes themselves are prone to oxidation and hydration. As an alternative we selected pyranosylnitromethanes (2,6-anhydro-1-deoxy-1-nitroalditols) as the starting material, and we now report that they can readily be converted directly and in high yield to the corresponding carbaldoximes by stannate(II)-mediated reduction.

RESULTS AND DISCUSSION

The approach adopted is illustrated in Sch. 1 for the conversion of L-fucose to tri-*O*-acetyl-β-D-fucopyranosylformaldoxime (**1**).[6] It involves base-catalyzed addition of nitromethane to the parent monosaccharide, acetylation of the resulting pyranosyl-nitromethane **2** to form its triacetate derivative **3**, and finally reduction of the nitromethyl moiety to the corresponding oxime.



2 R = H
3 R = Ac

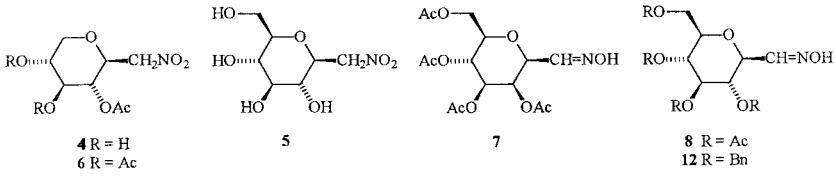
1

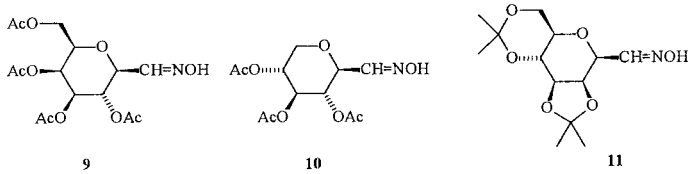
Scheme 1. Reagents: (i) $MeNO_2$, NaOMe/MeOH; (ii) Ac_2O, CF_3SO_3H; (iii) $SnCl_2$, PhSH, Et_3N.

L-Fucose was converted into β-L-fucopyranosylnitromethane (**2**) using the general procedure described by Köll et al.[7] for analogues such as D-xylose- and D-glucose-derived compounds **4** and **5**, which involves base-catalyzed addition of nitromethane (the Fischer Sowden reaction) and heating the resulting adduct to achieve dehydration and cyclization.[8,9] Treatment of compound **2** with Ac_2O/CF_3SO_3H afforded the tri-acetate derivative **3** in good yield (90%). In our hands, however, the isolated yields of the unprotected pyranosylnitromethanes, including **2**, were variable and rarely exceeded 40%. We have therefore adopted a protocol in which the unprotected nitromethyl compound is not isolated, and the crude product is acetylated using Ac_2O/CF_3SO_3H. By this means gram quantities of compound **3** could readily be prepared from the parent monosaccharide in 60–70% overall yield. Other per-*O*-acetyl-pyranosylnitromethanes were prepared similarly; for example the D-xylo-pyranosyl compound **6** (68%) from D-xylose.

The method selected for the conversion of the nitromethyl moiety to the carbaldoxime is based on that reported by Bartra et al.[10] which depends on the reducing ability of the stannate species $(PhS)_3Sn^-$. Treatment of tin(II) chloride (1.5 equiv.) in THF at 0°C with triethylamine (5 equiv.) and thiophenol (4.5 equiv.) afforded a yellow solution of the stannate complex $[Et_3NH][(PhS)_3Sn]$, to which was added a solution of nitromethylfucose compound **3** (1 equiv.) in THF. After stirring for 16 h and removal of the solvent and excess thiophenol, chromatography and crystallisation afforded tri-*O*-acetyl-β-L-fucopyranosylformaldoxime (**1**) as a 7:1 mixture of *E*- and *Z*-isomers in 90% combined yield. The overall yield from L-fucose to oxime **3** was 63%. The product was identified from its spectroscopic properties. In the ^1H NMR spectrum there are, in addition to the expected signals for the fucopyranosyl ring protons, characteristic signals for the 1-H protons of the *E*- and *Z*-isomers at 7.33 ($J_{1,2}$ 6.9 Hz) and 6.75 ppm respectively, and corresponding singlet peaks at 8.32 and 8.62 ppm for the OH groups. The procedure appears to be generally applicable for pyranose-1-carbaldoximes. D-Mannose-derived oxime **7** was prepared similarly in 76% yield from tetra-*O*-acetyl-β-D-mannopyranosylnitromethane; and likewise for the oximes **8** (76%), **9** (89%) and **10** (83%) prepared, respectively, from the nitromethane adducts of D-glucose, D-galactose and D-xylose.

A similar approach can be employed for pyranosyl oximes bearing ketal and benzyl ether protecting groups. 2,3:4,6-Di-*O*-isopropylidene-D-mannopyranosyl and 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl oximes **11** and **12** were prepared from the corresponding nitromethyl compounds in 80% and 65% yield, respectively.





The structure of D-mannose-derived oxime **7**, and the β-configuration at the anomeric centre in particular, were confirmed by X-ray crystallography (Fig. 1). A noteworthy feature of the crystal structure is the disorder in the region of the oxime moiety. There are two distinct arrangements represented by O1-N1-C1-C2 and O1′-N1′-C1-C2, corresponding to the *Z*- and *E*-oxime configurations. Thus both isomers detected in solution by NMR spectroscopy are incorporated within the crystal lattice. The ratio in the crystal, however, is 75% *Z*:25% *E*, whereas the *E*-isomer predominates in solution.

The structure is as expected for a β-D-mannopyranosyl compound. The Cramer and Pople puckering parameters[11] [$Q = 0.580$ Å, $\theta = 3.5^\circ$, $\phi = 228.7^\circ$] for the six-membered ring comprising C2-C3-C4-C5-C6-O6 show that it adopts a predominantly $^5C_2$ conformation. In particular, the θ value of 3.5° is close to the theoretical value for the chair conformation ($\theta = 0^\circ$). This arrangement is reflected in the ^{1}H NMR couplings involving the ring hydrogens [$J_{2,3}$ 1.1, $J_{3,4}$ 3.3, $J_{4,5}$ 10.1, $J_{5,6}$ 10.0 Hz]. For the oxime moiety, the observed ^{1}H NMR couplings of 5.5 and 4.1 Hz between 1-H of the oxime and 2-H of the pyranose ring are also consistent with the torsion angles in the crystal of 129.8° and 144.8° for H1-C1-C2-H2 and H1′-C1-C2-H2, suggesting that for both isomers the conformation in solution is broadly similar to that in the crystal.

In summary, an efficient procedure has been developed for the preparation of pyranosylcarbaldoximes which involves initial base-catalyzed addition of nitromethane to the parent hexose or pentose, peracetylation of the resulting pyranosylnitromethane, and finally reduction with tin(II) chloride/thiophenol/triethylamine. The overall yield for the sequence from the parent sugar to the oxime is typically 40–65%.

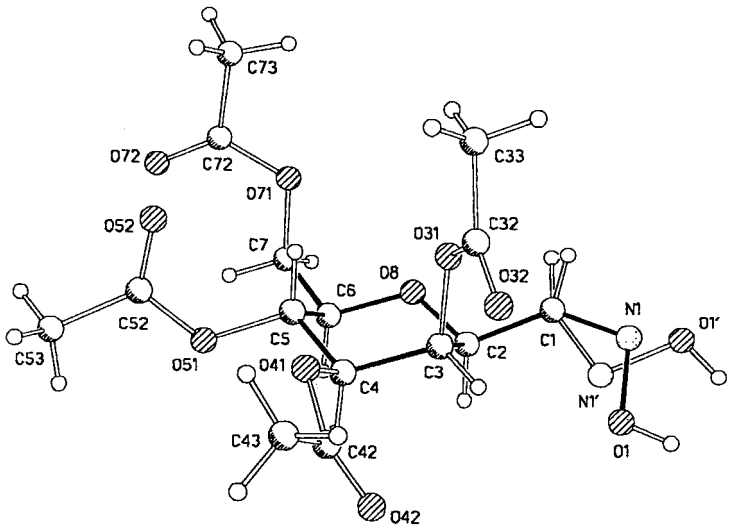


Figure 1. Structure of oxime **7**, showing the presence of both *E*- and Z-isomers.

EXPERIMENTAL

Typical Procedures

Tri-*O*-acetyl-β-L-fucopyranosylnitromethane (3). To a stirred suspension of L-fucose (600 mg, 3.7 mmol) in nitromethane (2 mL, 36.5 mmol) and methanol (2 mL) was added sodium methoxide (1 equiv.) in methanol, and the mixture stirred for 16 h. The resulting solid was isolated by filtration, washed with cold methanol, and dissolved in cold water. After passing through an amberlite IR (H^+) ion exchange column, the solution was concentrated in vacuo to remove the excess nitromethane. The resulting solution was heated under reflux for ~16 h, treated with activated charcoal, and refluxed for a further 2 h. After filtration to separate the charcoal, the solvent was removed in vacuo to afford an oil, which was treated under nitrogen with dry acetic anhydride (100 equiv.) and a catalytic amount of trifluoromethanesulfonic acid (0.1 mL), and the mixture stirred for ~16 h. The solution was poured onto ice cold water and the product extracted into chloroform (3×20 mL), the organic portion dried ($MgSO_4$), and the solvent removed in vacuo. The crude syrup formed was coevaporated with toluene (3×10 mL) and the solvent removed in vacuo to afford compound **3** (800 mg, 70%). M.p. 127–128°C

(from EtOH) (Found: C, 46.85; H, 5.47; N, 3.85. $C_{13}H_{20}NO_9$ requires C, 46.85; H, 5.75; N, 4.20) $[\alpha]_D^{18}$ −35.0 ($c = 1.0$, $CHCl_3$). ^{1}H NMR δ_H (250 MHz, $CDCl_3$) 1.14 (3H, d, 7-H), 1.97, 2.06, 2.16 (9H, 3 × s, $COCH_3$), 3.83 (1H, dq, 6-H), 4.20 (1H, ddd, 2-H), 4.35 (1H, dd, 1a-H), 4.54 (1H, dd, 1b-H), 5.02–5.12 (2H, m, 3-H, 4-H), 5.27 (1H, dd, 5-H); J/Hz 1a-1b 13.3, 1a-2 2.7, 1b-2 9.2, 4-5 2.7, 5-6 1.1, 6-7 6.4. ^{13}C NMR δ_C (63 MHz, $CDCl_3$) 16.0 (C-7), 20.5, 20.5, 20.6 ($COCH_3$), 66.7, 70.2, 71.8, 73.0, 74.6 (C-2 C-6), 76.1 (C-1), 169.9, 170.0, 170.3 ($COCH_3$). HRMS (FAB) Found: M^++1, 334.11398. $C_{13}H_{20}NO_9$ requires M^++H 334.11381.

Tri-*O*-acetyl-β-L-fucopyranosylformaldoxime (1). Triethylamine (0.2 mL, 1.5 mmol) and thiophenol (0.14 mL, 1.35 mmol) were added to a solution of tin(II) chloride (100 mg, 0.45 mmol) in dry THF (6 mL) under nitrogen at 0°C. To the resulting solution was added a solution of tri-*O*-acetyl-β-L-fucopyranosylnitromethane (**3**) (100 mg, 0.3 mmol) and the mixture stirred for 16 h. After removal of the solvent in vacuo, the resulting semi-crystalline residue was washed with hexane to remove excess PhSH, and the product separated by dry-flash chromatography (silica, hexane/Et_2O gradient elution) to afford compound **1** (82.6 mg, 90%) as a 7:1 mixture of *E*- and *Z*-isomers. M.p. 37–39°C. *E*-isomer: $[\alpha]_D^{18}$ −22 ($c = 1.0$, $CHCl_3$). ^{1}H NMR δ_H (250 MHz, $CDCl_3$) 1.17, (3H, d, 7-H), 1.97, 2.00, 2.17, (9H, s, $COCH_3$), 3.98 (1H, dd, 2-H), 5.07, (1H, dd, 4-H), 5.13–5.27, (2H, m, 3-H & 5-H), 7.33, (1H, d, 1-H), 8.54, (1H br s, NOH); $J(x, y)$/Hz 1-2 6.9, 2-3 9.7, 3-4 10.2, 4-5 3.3, 5-6 1.0, 6-7 6.4. ^{13}C NMR δ_C (63 MHz, $CDCl_3$) 16.2 (C-7), 20.5, 20.6 ($COCH_3$), 66.8, 70.4, 71.7, 72.9, 75.9, (C-2–C-6), 147.2 (C-1), 169.9, 170.1. 170.6 ($COCH_3$). HRMS (FAB): Found M^++1, 318.1180, $C_{13}H_{30}NO_8$ requires 318.11889. The isomer ratio was determined by comparison of the 1-H peaks at 7.33 and 6.75 ppm.

The following pyranosylcarbaldoximes were prepared similarly:

Tetra-*O*-acetyl-β-D-mannopyranosylformaldoxime (7). 89% prepared as a 2.3:1 mixture of *E*/*Z* isomers from tetra-*O*-acetyl-β-D-mannopyranosylnitromethane.[7] M.p. 154–156°C (from hexane/Et_2O) (lit.[2] 152–154°C). *E*-isomer: ^{1}H NMR δ_H (360 MHz, $CDCl_3$) 1.96, 2.03, 2.07, 2.13 (12H, s, $COCH_3$), 3.68 (1H, ddd, 6-H), 4.24 (1H, dd, 7a-H), 4.13 (1H, dd, 7b-H), 4.33 (1H, d, 2-H), 5.08 (1H, dd, 4-H), 5.22 (1H, dd, 5-H), 5.49 (1H, dd, 3-H), 7.30 (1H, d, 1-H), 8.53 (1H, br s, NOH); $J(x,y)$/Hz 1-2 5.5, 2-3 1.1, 3-4 3.3, 4-5 10.1, 5-6 9.8, 6-7a 2.2, 6-7b 5.6, 7a-7b 12.4. ^{13}C NMR δ_C (63 MHz, $CDCl_3$) 20.5, 20.5, 20.6 (4 × $COCH_3$), 62.5 (C-7), 65.5, 69.3, 71.7, 74.5, 76.2 (C-2 − C-6), 146.1 (C-1) 169.6, 170.1, 170.2, 170.8 ($COCH_3$). Selected data for *Z*-isomer: ^{1}H NMR δ_H (360 MHz, $CDCl_3$) 1.95, 2.03, 2.08, 2.11 (12H, s, $COCH_3$), 3.72 (1H, ddd, 6-H), 4.24 (1H, dd, 7a-H), 4.13 (1H, dd, 7b-H), 4.85 (1H, d, 2-H),

5.12 (1H, dd, 4-H), 5.22 (1H, dd, 5-H), 5.81 (1H, dd, 3-H), 6.69 (1H, d, 1-H), 7.79 (1H, br s, NOH); $J(x,y)$/Hz 1-2 4.1, 2-3 1.1, 3-4 3.4, 4-5 10.1, 5-6 9.9, 6-7a 2.2, 6-7b 5.5, 7a-7b 12.4.

Tetra-*O*-acetyl-β-D-glucopyranosylformaldoxime (8). 76% prepared as a 5:1 mixture of *E*/*Z* isomers from tetra-*O*-acetyl-β-D-glucopyranosylnitromethane.[7] M.p. 139–140°C (from hexane/Et_2O) (lit.[2] 155–157°C).

Tetra-*O*-acetyl-β-D-galactopyranosylformaldoxime (9). 89% prepared as a 9:1 mixture of *E*/*Z* isomers from tetra-*O*-acetyl-β-D-galactopyranosylnitromethane.[7] M.p. 184–185° (from hexane/Et_2O) (lit.[2] 170–172°C).

Tri-*O*-acetyl-β-D-xylopyranosylformaldoxime (10). 83% from tri-*O*-acetyl-β-D-xylopyranosylnitromethane (**6**).[7] M.p. 135–137°C (from hexane/Et_2O) (lit.[2] 160–163°C).

2,3:4,6-Di-*O*-isopropylidene-β-D-mannopyranosylformaldoxime (11). 80% prepared as a 1.6:1 mixture of *E*/*Z* isomers from 2,3:4,6-di-*O*-isopropylidene-β-D-mannopyranosylnitromethane.[12] M.p. 147–148°C (from hexane/Et_2O). *E*-isomer: ^{1}H NMR δ_H (250 MHz, $CDCl_3$) 1.32, 1.41, 1.40, 1.54 (12H, s, CH_3), 3.12-3.24 (1H, m, 6-H), 3.70–3.80 (2H, m, 5-H, 7b-H), 3.92 (1H, dd, 7a-H), 4.08 (1H, dd, 4-H), 4.22 (1H, dd, 3-H), 4.40 (1H, dd, 2-H), 7.52 (1H, d, 1-H), 8.49 (1H, br s, NOH); $J(x,y)$/Hz 1-2 6.6, 2-3 2.7, 3-4 5.3, 4-5 7.9, 5-6 nd, 6-7a 5.6, 6-7b 10.0, 7a-7b 10.9. ^{13}C NMR δ_C (63 MHz, $CDCl_3$) 18.6, 26.2, 28.2, 28.8 (CH_3), 61.6 (C-7), 69.6, 72.4, 74.3, 75.2, 75.8 (C-2 – C-6), 99.7, 110.1 (CMe_2), 147.6 (C-1). *Z*-isomer: ^{1}H NMR δ_H (250 MHz, $CDCl_3$) 1.32, 1.41, 1.40, 1.53 (12H, s, CH_3), 3.12–3.24 (1H, m, 6-H), 3.70–3.80 (2H, m, 5-H, 7b-H), 3.91 (1H, dd, 7a-H), 4.08 (1H, dd, 4-H), 4.57 (1H, dd, 3-H), 5.02 (1H, dd, 2-H), 6.84 (1H, d, 1-H), 8.84 (1H, br s, NOH); $J(x,y)$/Hz 1-2 4.7, 2-3 2.7, 3-4 5.3, 4-5 7.9, 5-6 nd, 6-7a 5.6, 6-7b nd, 7a-7b 10.9. ^{13}C NMR δ_C (63 MHz, $CDCl_3$) 18.6, 26.1, 28.2, 28.8 (CH_3), 61.6 (C-7), 69.3, 70.6, 72.6, 73.2, 75.5 (C-2–C-6), 99.7, 109.9 (CMe_2), 148.3 (C-1). HRMS (FAB): Found: M^++1, 288.14549, $C_{13}H_{22}NO_6$ requires 288.14471.

Tetra-*O*-benzyl-β-D-glucopyranosylformaldoxime (12). 65% prepared as a 4.2:1 mixture of *E*/*Z* isomers from 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylnitromethane.[13] M.p. 127–128°C (from hexane/Et_2O). ^{1}H NMR δ_H (250 MHz, $CDCl_3$) 3.53–4.06 (7H, m, 1-H – 7H), 4.55–5.05 (8H, m, $PhCH_2$), 6.85 (0.2H, d, $J_{1,2}$ 7.0 Hz, 1-H *Z*-isomer), 7.18–7.45 (20.8H, m, PhH & 1-H *E*-isomer), 8.42 (0.8H, br s, NOH *E*-isomer), 8.74 (0.2H, br s, NOH *Z*-isomer). ^{13}C NMR δ_C (63 MHz, $CDCl_3$) 68.8 (C-7), 73.7, 75.1, 75.3, 75.9 ($PhCH_2$), 77.0, 77.9, 79.0, 80.0, 86.7 (C-2 – C-6), 128.3, 128.4, 128.8, 128.9 (20 × PhCH), 138.0, 138.3, 138.4, 138.9 (PhC), 148.9 (C-1 *E*-isomer), 149.2 (C-1 *Z*-isomer). HRMS (FAB): Found: M^++1, 568.26725, $C_{35}H_{37}NO_6$ requires 568.26991.

Crystal structure of oxime 6. Crystal data for $C_{15}H_{21}NO_{10}$, orthorhombic, space group $P2_12_12_1$, $a = 8.179(2)$, $b = 10.831(2)$, $c = 20.801(7)$ Å, $V = 1842.8(9)$ Å^3. Data collected with Cu–Kα radiation on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 220K. The structure was solved by direct methods[14] and refined by full matrix least squares against F^2 (Shelxtl). Disorder in the structure is discussed in the text. Bond distances and angles in the disordered moiety were restrained to be similar; only the major component was refined anisotropically. $R1 = 6.11\%$ [based on F and 1496 data with $F > 4\sigma(F)$], $wR^2 = 16.94\%$ (based on F^2 and all 1899 data) for 244 parameters. The final difference map max and min. were 0.31 and -0.22 eÅ^{-3}, respectively. Full details of the structure have been deposited at the CCDC, reference number 147968.

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