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Preliminary communication

Acetylated 1-cyano and 1-cyano-2-hydroxy derivatives of D-galactal and D-arabinal

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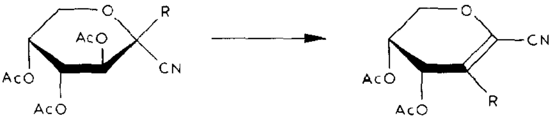
Glycals and 2-hydroxyglycals[1] are useful compounds because of their versatile reactivity, and 1-nitro-[2], 1-sulfonyl-[3], 1-formyl-, and 1-hydroxymethyl-glycals[4] have been described.

In seeking to prepare 1-cyanoglycals, 2,3,4,6-tetra-*O*-acetyl-1-bromo-D-galactopyranosyl cyanide (**1**) and its D-*arabino* analogue[5] (**5**) were each treated with zinc dust in acetic acid. The glycosyl cyanides **2** and **6** and their C-1 epimers, respectively, were isolated subsequently by crystallization from ethanol[6], but the yields were poor. ^{1}H-N.m.r spectroscopy of the reaction mixtures revealed the presence of the expected 1-cyanoglycals in addition to the glycosyl cyanides, and the ratios of the elimination products and the α and β anomers were 21:59:20 from **1** and 55:25:20 from **5**. Chromatography of the components of these mixtures was not efficient because of the similar R_F values.

1 R = Br
2 R = H

3 R = H
4 R = OAc



5 R = Br
6 R = H

7 R = H
8 R = OAc

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When solutions of **1** or **5** in benzene were boiled in the presence of excess of zinc and 1 mol of pyridine, the unsaturated compounds were formed rapidly (t.l.c. showed that **1** or **5** had disappeared after 5 min). 4,5,7-Tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*lyxo*-hept-2-enononitrile (**3**, 76%) from **1** had m.p. 113–115° (from ethanol), $[\alpha]_D^{20}$ −52° (*c* 1.3, chloroform). ^{1}H-N.m.r. data (C_6D_6): δ 4.87 (dd, 1 H, $J_{3,4}$ 1.75, $J_{3,5}$ 2.5 Hz, H-3), 5.20 (ddd, 1 H, $J_{4,5}$ 4.5, $J_{4,6}$ 1.5 Hz, H-4), 5.14 (ddd, 1 H, $J_{5,6}$ 2.5 Hz, H-5), 3.56 (m, 1 H, H-6), 3.91–4.00 (2 s, 2 H, H-7,7′), 1.55–1.63 (3 s, 9 H, 3 Ac).

Anal. Calc. for $C_{13}H_{15}NO_7$: C, 52.52; H, 5.08; N, 4.71. Found: C, 52.14; H, 5.16; N, 4.53.

4,5-Di-*O*-acetyl-2,6-anhydro-3-deoxy-D-*erythro*-hex-2-enononitrile (**7**, 75%) from **5** had m.p. 94–95° (from ethanol), $[\alpha]_D^{20}$ +176° (*c* 1.2, chloroform). ^{1}H-N.m.r. data (C_6D_6): δ 4.98 (dd, 1 H, $J_{3,4}$ 4, $J_{3,5}$ 0.7 Hz, H-3), 5.15 (ddd, 1 H, $J_{4,5}$ 4, $J_{4,6'}$ 1.5 Hz, H-4), 4.88 (m, 1 H, $J_{5,6}$ 6.75 Hz, H-5), 3.26 (ddd, 1 H, $J_{5,6'}$ 2.75 Hz, H-6′), 3.53 (dd, 1 H, $J_{6,6'}$ 11.75 Hz, H-6), 1.59, 1.64 (2 s, 6 H, 2 Ac).

Anal. Calc. for $C_{10}H_{11}NO_5$: C, 53.33; H, 4.92; N, 6.21. Found: C, 52.92; H, 4.81; N, 6.15.

Reaction of **1** or **5** with 1 mol of mercury(II) cyanide in refluxing nitromethane in the presence of catalytic amounts of silver triflate was complete within 5 min (t.l.c.). 3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-D-*lyxo*-hept-2-enononitrile (**4**, 81%) from **1** had m.p. 99–101° (from ethanol), $[\alpha]_D^{20}$ −68° (*c* 1.2, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.96 (dd, 1 H, $J_{4,5}$ 4.6, $J_{4,6}$ 1 Hz, H-4), 5.53 (dd, 1 H, $J_{5,6}$ 1.5 Hz, H-5), 4.55 (m, 1 H, $J_{6,7}$ 6.3, $J_{6,7'}$ 6.3 Hz, H-6), 4.23–4.37 (2 s, 2 H, H-7,7′), 2.22–2.40 (4 s, 12 H, 4 Ac).

Anal. Calc. for $C_{15}H_{17}NO_9$: C, 50.70; H, 4.82; N, 3.94. Found: C, 50.08; H, 4.77; N, 3.91.

Column chromatography (benzene–ether–hexane, 6:3:1) on silica gel gave 3,4,5-tri-*O*-acetyl-2,6-anhydro-D-*erythro*-hex-2-enononitrile (**8**, 82%), R_F 0.39, $[\alpha]_D^{20}$ +162° (*c* 1.5, chloroform), from **5**. ^{1}H-N.m.r. data ($CDCl_3$): δ 5.82 (dd, 1 H, $J_{4,5}$ 4.5, $J_{4,6}$ 1.25 Hz, H-4), 5.32 (m, 1 H, $J_{5,6}$ 3.5 Hz, H-5), 4.21 (ddd, 1 H, $J_{6,6'}$ 11.25 Hz, H-6), 4.12 (dd, 1 H, $J_{5,6'}$ 8 Hz, H-6′), 2.12–2.22 (3 s, 9 H, 3 Ac).

Reactions of **1** on a 5–10-g scale were performed without difficulty.

The utility of the 1-cyanoglycals in synthesis is being investigated.

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