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Note

Synthesis and reactions of chlorodeoxy-L-idofuranoid derivatives

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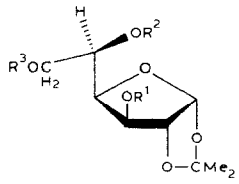
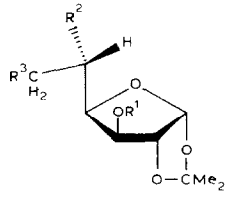
The introduction of halogen substituents at certain positions of the sucrose molecule greatly increases the sweetness[1–3]. Taste studies have been carried out mainly on derivatives of D sugars[3] with only one systematic study[4] of L sugars. The synthesis and reactions of chlorodeoxy-1,2-*O*-isopropylidene-L-idofuranoid derivatives is now described.

A convenient synthesis of L-idose is *via* sulphonate displacement of 5-*O*-tosyl derivatives of 1,2-*O*-isopropylidene-α-D-glucopyranose with acetate or benzoate ions[5–7]. The reaction of 3-*O*-acetyl-1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-glucofuranose with sodium benzoate in boiling *N*,*N*-dimethylformamide for 6 h yielded 50% of 3-*O*-acetyl-5,6-di-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-idofuranose[5], whereas the reaction of 6-*O*-benzoyl-1,2-*O*-isopropylidene-5-*O*-tosyl- or -3,5-di-*O*-tosyl-α-D-glucofuranose in *N*,*N*-dimethylformamide[6,7] involved both direct displacement and neighbouring-group participation. Treatment of 3-*O*-acetyl-1,2-*O*-isopropylidene-5,6-di-*O*-mesyl-α-D-glucofuranose (**1**) with acetate (or benzoate) in hexamethylphosphoric triamide at ~90° gave, after ~2 weeks, in addition to the corresponding L-idofuranose derivative **2** (or **3**) (~54%), ~35% of the 5-acetate **4** (or 5-benzoate **5**) of 3,6-anhydro-1,2-*O*-isopropylidene-β-L-idofuranose (**6**). Treatment of **4** or **5** with methanolic sodium methoxide yielded 1,2-*O*-isopropylidene-β-L-idofuranose (**7**).

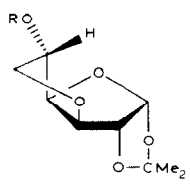
The initial displacement of MsO-6 of **1** by acetate or benzoate to give **8** and **9**, respectively, was observed after ~3.5 h (61–68% yield). When the reaction was carried out in the presence of 18-Crown-6 in either acetonitrile or *N*,*N*-dimethylformamide at ~70° under nitrogen, **8** and **9** were obtained in > 80% yield after ~2 h. However, no displacement of MsO-5 was observed in acetonitrile even after boiling for 36 h. In *N*,*N*-dimethylformamide at 120°, displacement of MsO-5 by both potassium acetate and benzoate occurred after ~52 h to form ~67% of **2** and ~69% of **3**, respectively, together with ~24% of the 3,6-anhydro-β-L-idofuranose derivatives. However, 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-mesyl-α-D-gluco-



1 R^1 = Ac, R^2 = R^3 = Ms
8 R^1 = R^3 = Ac, R^2 = Ms
9 R^1 = Ac, R^2 = Ms, R^3 = Bz



2 R^1 = Ac, R^2 = R^3 = OAc
3 R^1 = Ac, R^2 = R^3 = OBz
7 R^1 = H, R^2 = R^3 = OH
10 R^1 = Ac, R^2 = Cl, R^3 = OBz
11 R^1 = Bz, R^2 = Cl, R^3 = OBz
12 R^1 = H, R^2 = Cl, R^3 = OH
13 R^1 = H, R^2 = OH, R^3 = Cl



4 R = Ac
5 R = Bz
6 R = H

furanose was not detected although the corresponding 5-tosylate was reported[5] when the displacement reaction was carried out in aqueous 95% 2-methoxymethanol.

The structures of **4** and **6** were confirmed on the basis of the ^{1}H- and ^{13}C-n.m.r. data. In the ^{1}H-n.m.r. spectra of **4** and **6**, the H-3,4 resonances appeared as two doublets ($J_{3,4}$ 2.4, $J_{4,5}$ 0 Hz), consistent with the L-*ido* configuration[8]. These signals for the corresponding D-*gluco* derivatives appeared as a doublet and a triplet, respectively ($J_{3,4}$ 3.9, $J_{4,5}$ 3.9 Hz)[9]. The ^{13}C resonances of the carbons involved in the anhydro ring of **4** and **6** were at higher field (C-3, 5-8; C-6, ~13 p.p.m.) than those of C-3 and C-6 of **2**.

Treatment of the 3,6-di-*O*-acetyl-5-*O*-mesyl derivative **8** with potassium acetate in *N*,*N*-dimethylformamide also gave **4**. Therefore, the 3,6-anhydro-L-idofuranose derivative **4** could not have arisen *via* an initially formed 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-mesyl-α-D-glucofuranose followed by displacement of MsO-5. Various amounts or **4** were formed when the triacetate **2** was heated in pyridine or *N*,*N*-dimethylformamide. Furthermore, a substantial amount of **4** was formed when 1,2-*O*-isopropylidene-β-L-idofuranose (**7**) was treated with sulphuryl chloride (see below), and 5,6-dichloro-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-idofuranose readily formed 3,6-anhydro-5-chloro-5-deoxy-L-idofuranose instead of the expected 5,6-dichloro-5,6-dideoxy-L-idofuranose when treated with acid[8]. Molecular models showed that, in the L-*ido* configuration, steric effects due to the 5-substituent cause the 6-substituent to occupy a position adjacent to AcO-3 such that it is sterically disposed for HO-3 (arising from hydrolysis of the acetyl group) to attack AcO-6 from the rear.

The reaction of **8** with lithium chloride in *N*,*N*-dimethylformamide in the presence of 18-Crown-6 smilarly yielded 65% of crystalline 3-*O*-acetyl-6-*O*-bezoyl-5-chloro-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (**10**). Compound **10** was converted into a crystalline benzoate (**11**) by first obtaining 5-chloro-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (**12**), using methanolic 0.1M sodium methoxide.

The mass spectra of **10** and **11** clearly reflected the chloro substituent, as indicated by the $[M^+ - 15]$ fragments at *m/z* 369 and 431 (ratio 3:1). The resonances in the ^{1}H-n.m.r. spectra of **10–12** were not well resolved. However, reaction of **12** with trichloroacetyl isocyanate resulted in the appearence of singlets at δ 8.95 and 9.03 due to the NH groups of the resulting dicarbamate; H-3 and H-6 were deshielded by ~1.2 and ~0.6 p.p.m., respectively, thereby indicating the positions of the hydroxyl groups in **12**. Furthermore, the ^{13}C resonances of C-5 of **10–12** were shifted upfield by >10 p.p.m. with respect to C-5 for the triacetate **2**, confirming the presence of the 5-chloro substituent.

The reaction of 1,2-*O*-isopropylidene-β-L-idofuranose (**7**) with sulphuryl chloride (3.0 mequiv.), initially at ~ −55° and then for 1.5 h at 0°, gave, instead of the expected 6-chloro-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (**13**), 85% of the 3,6-anhydro derivative **6**. The 6-chloro derivative **13** was obtained when 1 mequiv. of sulphuryl chloride was used and the reaction mixture was worked-up after 0.5 h at ~ −45°.

The structure of **13** was confirmed from the n.m.r. and mass-spectral data. Accurate mass measurement showed a fragment ion at *m/z* 223, corresponding to $C_8H_{12}ClO_5$ (3:1 doublet). The resonances due to H-3,4,5,6 overlapped, but the spectrum of the trichloroacetylcarbamate derived from **13** contained two high-field NH singlets and the signals due to H-3 and H-5 were deshielded ~0.8 and ~1.2 p.p.m., respectively, thereby indicating the position of the hydroxyl groups in **13**. Furthermore, the signals for H-4,6,6′ could now be observed at δ 4.64, 3.89, and 3.69 (dd, $J_{4,5}$ 8.1, $J_{5,6}$ 3.7, $J_{5,6'}$ 4.5, $J_{6,6'}$ 13.0 Hz). The ^{13}C resonance of C-6 was shifted upfield by ~17 p.p.m. with respect to that for the triacetate **2**.

EXPERIMENTAL

For general experimental details, see ref. 1.

*Re-examination of replacement reactions of 3-*O*-acetyl-1,2-*O*-isopropylidene-5,6-di-*O*-methanesulphonyl-α-*D*-glucofuranose* (**1**). — (*a*) *With potassium acetate.* A solution of **1** (0.8 g) in *N*,*N*-dimethylformamide (10 mL) containing potassium acetate (1.0 g) was stirred for 5 h at ~70°. T.l.c. (toluene–ethyl acetate, 1:1) then revealed only one fast-moving compound. The solution was poured into ice–water, the precipitate was collected and washed well with cold water, and a solution in dichloromethane was dried ($MgSO_4$) and concentrated. The residue was recrystallised from ether to give **8** (0.45 g, 61.6%), m.p. 110–111°, $[\alpha]_D$ −13° (*c* 0.2, dichloromethane) (Found: C, 44.0; H, 5.8; S, 8.0 $C_{14}H_{22}O_{11}S$ calc.: C, 44.0; H, 5.8; S, 8.4%). N.m.r. data ($CDCl_3$): ^{1}H, δ 5.91 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.30 (d, 1 H, $J_{2,3}$ 0, $J_{3,4}$ 2.8 Hz, H-3), 5.07 (td, 1 H, $J_{4,5}$ 9.0, $J_{5,6}$ 2.2, $J_{5,6'}$ 6.1 Hz, H-5), 4.69 (dd, $J_{6,6'}$ 12.7 Hz, H-6), 4.52 (d, 1 H, H-2), 4.40 (s, 1 H, H-4), 4.21 (dd, 1 H, H-6′), 3.05 (s, 3 H, Ms), 2.13 and 2.17 (2 s, each 3 H, 2 Ac), 1.32 and 1.52 (2 s, 6 H, CMe_2); ^{13}C, δ 112.7 (s, CMe_2), 105.2 (s, C-1), 83.0 (s, C-2), 76.4 (s, C-3 or 4), 74.9 (s, C-4 or 3), 74.1 (s, C-5), 63.2 (s, C-6), 38.9 (s, CH_3SO_2), 26.2 and 26.8 [(2 s, $C(CH_3)_2$].

(*b*) With potassium benzoate. The reaction was carried out as in (*a*), using potassium benzoate (1.0 g), to yield **9** (68.5%), m.p. 119–120° (from ethanol), $[\alpha]_D$ −10.5° (*c* 0.5, dichloromethane) (Found: C, 51.7; H, 5.2; S, 7.6 $C_{19}H_{24}O_{10}S$ calc.: 51.35; H, 5.4: S, 7.2%). N.m.r. data ($CHCl_3$): ^1H, δ 7.2–8.1 (m, 5 H, Ph), 5.93 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.33 (d, 1 H, $J_{2,3}$ 0, $J_{3,4}$ 2.7 Hz, H-3), 5.26 (td, 1 H, $J_{4,5}$ 6.7, $J_{5,6}$ 2.2, $J_{5,6'}$ 6.1 Hz, H-5), 4.94 (dd, $J_{6,6'}$ 12.7 Hz, H-6), 4.3–4.6 (m, 3 H, H-2,4,6'), 2.95 (s, 3 H, Ac), 1.33 and 1.55 (2 s, 6 H, CMe_2); ^{13}C, δ 112.7 (s, CMe_2), 105.2 (s, C-1), 83.0 (s, C-2), 76.4 (s, C-3 or 4), 75.0 (s, C-4 or 3), 74.1 (s, C-5), 63.9 (s, C-6), 55.7 (s, CH_3SO_2), 26.2 and 26.6 [2 s, $C(CH_3)_2$].

(*c*) *With potassium acetate in the presence of 18-Crown-6.* *N*,*N*-dimethylformamide (65 mL) containing activated alumina (2 g) was stirred with potassium acetate (8.5 g) for 15 min. 18-Crown-6 (0.8 g) was added, followed by **1** (8.3 g). The mixture was heated for 2 h at ~70° under nitrogen, when t.l.c. (toluene–ethyl acetate, 1:1) showed only one fast-moving spot. The reaction was worked up as in (*a*) to yield 82% of **8**.

When the reaction was repeated with heating for ~52 h at 120° under nitrogen, t.l.c. (toluene–ethyl acetate, 3:2) revealed two major faster moving and one minor slower moving components. The mixture was diluted with anhydrous pyridine and treated with acetic anhydride (5 mL). Column chromatography (toluene–ethyl acetate, 6:1) of the syrupy product gave, first, 5-*O*-acetyl-3,6-anhydro-1,2-*O*-isopropylidene-β-L-idofuranose (**4**, 24.4%), m.p. 59–60° (from ethanol), $[\alpha]_D$ +30° (*c* 0.6, acetone) (Found: C, 53.85; H, 6.5 $C_{11}H_{16}O_6$ calc.: C, 54.1; H, 6.55%). N.m.r. data ($CDCl_3$): ^1H, δ 5.85 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.76 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.63 (d, 1 H, $J_{3,4}$ 2.4 Hz, H-3), 4.59 (d, 1 H, $J_{4,5}$ 0 Hz, H-4), 4.7–4.8 (m, 1 H, H-5), 4.01 (dd, 1 H, $J_{5,6}$ 3.2, $J_{6,6'}$ 10.0 Hz, H-6), 3.86 (dd, 1 H, $J_{5,6'}$ 1.2 Hz, H-6'), 2.08 (s, 3 H, Ac), 1.33 and 1.49 (2 s, 6 H, CMe_2); ^{13}C, δ 112.4 (s, CMe_2), 106.4 (s, C-1), 85.5 (2 s, C-2 and C-4), 84.1 (s, C-3), 77.1 (s, C-5), 76.8 (s, C-6), 27.3 and 26.6 [2 s, $C(CH_3)_2$].

Eluted second was 3,5,6-tri-*O*-acetyl-1,2-*O*-isopropylidene-β-L-idofuranose (**2**, 54.2%), m.p. 79–81° (from ether–light petroleum), $[\alpha]_D$ −15° (*c* 0.7, acetone); lit.[5] m.p. 82–84°, $[\alpha]_D$ −2° (chloroform).

(*d*) *With potassium benzoate in the presence of 18-Crown-6.* Reaction (*c*) was repeated using potassium benzoate. After ~50 h, t.l.c. (toluene–ethyl acetate, 3:1) revealed one fast and several slower components. Work-up in the usual manner afforded a syrupy product which was triturated with ethanol to give **3** (43%), m.p. 123–124°, $[\alpha]_D$ −19° (*c* 0.5, dichloromethane); lit.[5] m.p. 132–134°, $[\alpha]_D$ −21.5° (chloroform).

The filtrate was concentrated and the residue was treated with methanolic 0.1M sodium methoxide (5 mL). Column chromatography (toluene–ethyl acetate, 3:1) of the syrupy product gave, first, 3,6-anhydro-1,2-*O*-isopropylidene-β-L-idofuranose (**6**, 25.3%), m.p. 68–70° (from ethanol), $[\alpha]_D$ −17° (*c* 0.5, methanol) (Found: C, 53.55; H, 6.7. $C_9H_{14}O_5$ calc.: C, 53.5; H, 6.9%). N.m.r data ($CDCl_3$) ^1H, δ 5.85 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.63 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.76 (d, 1 H, $J_{3,4}$

2.4 Hz, H-3), 4.67 (d, 1 H, H-4), 4.3–4.4 (m, 1 H, H-5), 4.02 (dd, 1 H, $J_{5,6}$ 3.2, $J_{6,6'}$ 10.5 Hz, H-6), 3.86 (dd, 1 H, $J_{5,6'}$ 1.2 Hz, H-6'), 1.32 and 1.49 (2 s, 6 H, CMe_2); ^{13}C, δ 112.5 (s, CMe_2), 106.4 (s, C-1), 87.9 (s, C-2), 84.2, 78.5 (2 s, C-3,4), 75.0 (s, C-5), 74.9 (s, C-6), 27.3 and 26.7 [2 s, $C(CH_3)_2$].

Eluted second was 1,2-*O*-isopropylidene-β-L-idofuranose (**7**, 22%), m.p. 112–114° (from ether), $[\alpha]_D$ −22° (*c* 0.45, methanol); lit.[5] m.p. 112–113°, $[\alpha]_D$ −30° (water); lit.[10] m.p. 111–113°, $[\alpha]_D$ −19° (methanol).

3-O-Acetyl-6-O-benzoyl-5-chloro-5-deoxy-1,2-O-isopropylidene-β-L-idofuranose (**10**). — A mixture of *N,N*-dimethylformamide (15 mL), lithium chloride (2.1 g), and 18-Crown-6 (0.2 g) was stirred with **9** (2.1 g) for ~50 h at 120° under nitrogen, when t.l.c. (toluene–ethyl acetate, 3:1) revealed one fast major component and traces of several slow-moving components. Work-up in the usual way gave a syrupy product which crystallised from ether to give **10** (1.2 g, 66.2%), m.p. 143–144°, $[\alpha]_D$ −12° (*c* 0.5, dichloromethane) (Found: C, 56.7; H, 5.4; Cl, 8.9. $C_{18}H_{21}ClO_7$ calc.: C, 56.2; H, 5.5; Cl, 9.2). N.m.r. data ($CDCl_3$): ^1H, δ 7.2–8.1 (m, 5 H, Ph), 5.96 (1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.2–5.3 (m, 1 H, H-5), 4.4–4.6 (m, 5 H, H-2,3,4,6,6'), 2.07 (s, 3 H, Ac), 1.32, 1.53 (2 s, 6 H, CMe_2); ^{13}C, δ 112.5 (s CMe_2), 104.3 (s, C-1), 83.5 (s, C-2), 79.3 (s, C-4), 76.2 (C-3), 65.2 (s, C-6), 55.7 (s, C-5), 26.2 and 26.6 [2 s, $C(CH_3)_2$].

3,6-Di-O-*benzoyl-5-chloro-5-deoxy-1,2-O-isopropylidene-β-L-idofuranose* (**11**). — A methanolic solution of **10** (0.4 g in 10 mL) was treated with a catalytic amount of sodium methoxide for 15 min at room temperature. The solution was deionised with Duolite MB 5113 mixed-bed resin and concentrated to give syrupy **12** (0.22 g, 89%), $[\alpha]_D$ −16° (*c* 0.55, methanol) (Found: C, 45.35; H, 6.5; Cl, 15.1. $C_9H_{15}ClO_5$ calc.: C, 45.3; H, 6.3; Cl, 14.9%). N.m.r. data ($CDCl_3$–trichloroacetyl isocyanate): ^1H, δ 8.96 and 9.03 (2 s, NH of carbamate groups), 5.98 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 5.42 (s, 1 H, $J_{2,3}$ 0, $J_{3,4}$ 0 Hz, H-3), 4.74 (d, 1 H, H-2), 4.4–4.5 (m, 4 H, H-4,5,6,6'), 1.33 and 1.55 (2 s, 6 H CMe_2); ^{13}C, δ 112.1 (s, CMe_2), 104.3 (s, C-1), 85.3 (s, C-2), 83.1 (s, C-4), 74.4 (s, C-3), 63.3 (s, C-6), 59.5 (s, C-5), 26.2 and 26.7 [2 s, $C(CH_3)_2$].

Conventional treatment of **12** (0.2 g) with pyridine (5 mL) and benzoyl chloride (1 mL) at room temperature and recrystallisation of the product (0.3 g, 82%) from ether–light petroleum afforded **11**, m.p. 103–104°, $[\alpha]_D$ −43° (*c* 0.3, dichloromethane) (Found: C, 61.45; H, 5.1; Cl, 7.5. $C_{23}H_{23}ClO_7$ calc.: C, 61.8; H, 5.15, Cl, 7.95%). N.m.r. data ($CDCl_3$): ^1H, δ 7.2–8.0 (m, 10 H, 2 Ph), 6.02 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.99 (d, 1 H, $J_{2,3}$ 0, $J_{3,4}$ 2.5 Hz, H-3), 5.67 (d, 1 H, H-4), 5.5 (m, 1 H, H-5), 4.5–4.9 (m, 3 H, H-2, 6,6'), 1.33 and 1.57 (2 s, 6 H, CMe_2); ^{13}C, δ 112.6 (s, CMe_2), 104.4 (s, C-1), 83.7 (s, C-2), 78.8 (s, C-3 or 4), 76.8 (s, C-4 or 3), 65.9 (s, C-6), 55.5 (s, C-5), 26.3 and 26.8 [2 s, $C(CH_3)_2$].

6-Chloro-6-deoxy-1,2-O-isopropylidene-β-L-idofuranose (**13**). — To a solution of **7** (2.2 g) in pyridine (12 mL) and chloroform (12 mL) at ~ −50° was added sulphuryl chloride (1.1 mL) in cloroform (2 mL) dropwise during 15 min. The mixture was kept for 10 min at ~ −45°, when t.l.c. (toluene–ethyl acetate, 6:1)

revealed only one faster major compound. The mixture was poured into vigorously stirred, ice-cold, aqueous 10% sulphuric acid (20 mL) and extracted with dichloromethane (3 × 10 mL). The combined extracts were washed successively with water, saturated aqueous sodium hydrogencarbonate, and water, and then concentrated. A solution of the syrupy residue in methanol (15 mL) was stirred in an ice-bath and a few drops of 0.8% sodium iodide in water–methanol (1:1) were added. After stirring for 0.5 h, the solution was concentrated to dryness and the residue was recrystallised from ether–light petroleum to give **13** (1.5 g, 63.5%), m.p. 106–107°, $[\alpha]_D$ −31° (*c* 0.5, methanol) (Found: C, 45.6; H, 5.9; Cl, 15.3. $C_9H_{15}ClO_5$ calc: C, 45.3; H, 6.3; Cl, 14.9%). N.m.r. data ($CDCl_3$–trichloroacetyl isocyanate): ^1H, δ 8.83 and 9.35 (2 s, NH of carbamate groups), 5.97 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.78 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 5.30 (d, 3 H, $J_{3,4}$ 3.2 Hz, H-3), 4.64 (dd, 1 H, $J_{4,5}$ 8.1 Hz, H-4), 5.4–5.5 (m, 1 H, H-5), 3.89 (dd, 1 H, $J_{5,6}$ 3.7, $J_{6,6'}$ 13.0 Hz, H-6), 3.69 (dd, 1 H, $J_{5,6'}$ 4.5 Hz, H-6′), 1.32 and 1.54 (2 s, 6 H, CMe_2); ^{13}C, δ 112.2 (s, CMe_2), 104.7 (s, C-1), 85.5 (s, C-2), 78.2 (s, C-3 or 4), 76.7 (s, C-4 or 3), 70.9 (s, C-5), 45.8 (s, C-6), 26.3 and 26.9 [2 s, $C(CH_3)_2$].

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