Carbohydrate Research, 80 (1980) 45–51

SYNTHESIS OF L-IDOFURANURONO-6,3-LACTONE AND ITS DERIVATIVES *via* HEXODIALDODIFURANOSES*

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(Received February 15th, 1979; accepted for publication, July 9th, 1979)

ABSTRACT

1,2-*O*-Alkylidene-β-L-idofuranurono-6,3-lactones were obtained from the corresponding 5-*O*-toluene-*p*-sulphonyl-α-D-glucofuranurono-6,3-lactones by a sequence involving lactone reduction, benzoylation of HO-6, inversion of configuration at C-5, deacylation, and lactol oxidation. Hydrogenolysis or methanolysis of 1,2-*O*-benzylidene-β-L-idofuranurono-6,3-lactone gave L-idofuranurono-6,3-lactone and a mixture of its methyl glycosides, respectively.

INTRODUCTION

For our continuing investigations of hexuronic acids, L-idofuranurono-6,3-lactone and its methyl glycosides and 1,2-*O*-isopropylidene derivative were needed. Only the last was known hitherto, but because of the formation of intermediate diastereomers, each of the two syntheses[3–5] gave a low yield (7%). Moreover, after acid hydrolysis of 1,2-*O*-isopropylidene-β-L-idofuranurono-6,3-lactone, L-iduronic acid (22.3%) was the only compound isolated[3].

The preparation of D-manno-[6] and L-gulo-furanurono-6,3-lactone[1] from the corresponding D-*gluco* isomer suggested that L-iduronic acid derivatives should be obtainable from the same starting compound.

RESULTS AND DISCUSSION

Three approaches to the D-*gluco*→L-*ido* inversion were considered.

The first approach involved esterification of 1,2-*O*-alkylidene-α-D-glucofuranurono-6,3-lactones with simultaneous inversion in the presence of a redox catalyst[7]. Although 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose, in the presence of triphenylphosphine, diethyl azodicarboxylate, and benzoic acid, yielded 3,6-anhydro-5-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-idofuranose, 1,2-*O*-alkylidene-α-D-glucofuranurono-6,3-lactones gave intractable product mixtures under similar conditions.

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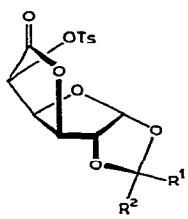
*Reactions of D-Glucuronic Acid: Part XIII. For Part XII, see ref. 1.



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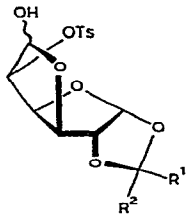
10 $R^1 = Ph, R^2 = H$



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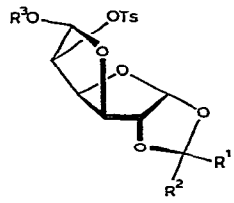
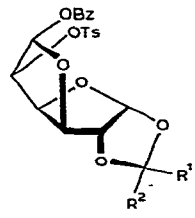


3 $R^1 = R^2 = Me$, $R^3 = Bzl$
4 $R^1 = R^2 = Me$, $R^3 = Bz$
12 $R^1 = Ph$, $R^2 = H$, $R^3 = Bz$



5 $R^1 = R^2 = Me$
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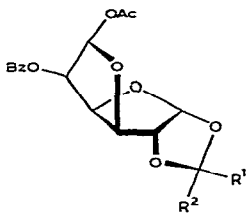

6 $R^1 = R^2 = Me$
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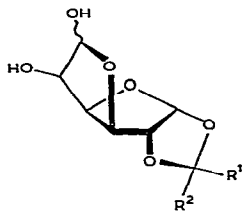

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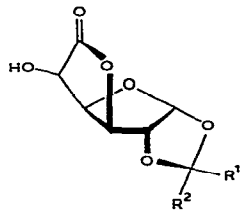

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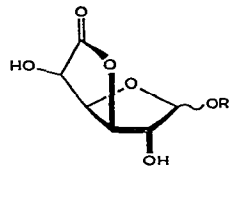
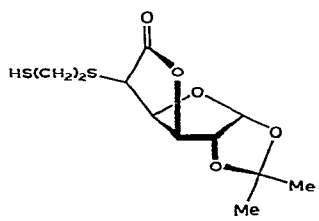
16 $R^1 = Ph, R^2 = H$



9 R = H
9a R = Me



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The second approach involved nucleophilic substitution of 1,2-*O*-alkylidene-5-*O*-toluene-*p*-sulphonyl-α-D-glucofuranurono-6,3-lactones by oxygen nucleophiles, without protection of the lactone group or after its transformation into an ortho ester. However, treatment of 1,2-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-α-D-glucofuranurono-6,3-lactone (**1**) with various nucleophiles (benzoate, acetate) and solvents (acetone, acetic anhydride, *N,N*-dimethylformamide, and hexamethylphosphoric triamide) invariably led to extensive decomposition. Attempts to protect the lactone ring in **1** were unsuccessful. No formation of ortho ester could be observed with Meerwein's salt[8], and Corey's method[9] yielded 1,2-*O*-isopropylidene-5-*S*-(2-mercaptoethyl)-5-thio-β-L-idofuranurono-6,3-lactone (**17**) as the only isolable product.

The third approach involved lactone reduction, appropriate protection of the

resulting lactol, and inversion of configuration at C-5 by a neighbouring-group reaction and re-oxidation. Thus, 6-*O*-benzoyl-1,2-*O*-isopropylidene- (**4**) and 6-*O*-benzoyl-1,2-*O*-benzylidene-5-*O*-toluene-*p*-sulphonyl-(6*R*)-α-D-*gluco*-hexodialdo-1,4:6,3-difuranose (**12**), on treatment with acetate, gave 6-*O*-acetyl-5-*O*-benzoyl-1,2-*O*-isopropylidene- (**6**) and 6-*O*-acetyl-5-*O*-benzoyl-1,2-*O*-benzylidene-(6*S*)-β-L-*ido*-hexodialdo-1,4:6,3-difuranose (**14**), respectively. The inertness under these reaction conditions of the (6*S*)-isomers **5** and **13** and of benzyl 1,2-*O*-isopropylidene- (**3**) and methyl 1,2-*O*-benzylidene-5-*O*-toluene-*p*-sulphonyl-(6*S*)-α-D-*gluco*-hexodialdo-1,4-furanose-6,3-furanoside[1] unequivocally proved the occurrence of neighbouring-group participation involved in the conversions **4**→**6** and **12**→**14**.

Deacylation of **6** and **14** yielded 1,2-*O*-isopropylidene- (**7**) and 1,2-*O*-benzylidene-β-L-*ido*-hexodialdo-1,4:6,3-difuranose (**15**), respectively.

Unlike 1,2-*O*-alkylidenehexofuranoses[10,11], **7** and **15** as well as methyl (6*S*/6*R*)-D-*gluco*-hexodialdo-1,4-furanose-6,3-furanoside[1] were readily oxidised under neutral conditions to the respective hexofuranurono-6,3-lactones **8** and **16**.

The third approach avoids the separation of diastereomers, and not only gives yields (28%, from D-glucofuranurono-6,3-lactone) of 1,2-*O*-isopropylidene-β-L-idofuranurono-6,3-lactone substantially higher than those previously reported, but also allows, for the first time, the isolation of L-idofuranurono-6,3-lactone by hydrogenolysis of its 1,2-*O*-benzylidene derivative.

EXPERIMENTAL

General methods. — Melting points were determined with a Tottoli apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. T.l.c. was performed on silica gel 60 F_{254} pre-coated aluminum sheets (Merck). N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si), unless stated otherwise, in the pulsed Fourier-transform mode with a Bruker WH-90 DS instrument.

*Benzyl 1,2-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-(6*S*)-α-D-gluco-hexodialdo-1,4-furanose-6,3-furanoside* (**3**). — A mixture of 1,2-*O*-isopropylidene-5-*O*-toluene-*p*-sulphonyl-α-D-*gluco*-hexodialdo-1,4:6,3-difuranose* (**2**; 1.12 g, 3 mmol), benzyl bromide (1 ml, 8 mmol), silver oxide (1.1 g, 8 mmol), and toluene (120 ml) was stirred at room temperature for 6 h; the reaction was monitored by t.l.c. The syrup obtained after filtration and concentration of the mixture was triturated with light petroleum (100 ml), to yield **3** (1.2 g, 86.5%), m.p. 115–116.5° (from ethanol), $[\alpha]_D^{20}$ +89° (*c* 1.6, chloroform), R_F 0.68 (benzene–ethyl acetate, 10:1). N.m.r. data: δ 1.34 and 1.44 (2 s, 6 H, CMe_2), 2.44 (s, 3 H, Me of Ts), 4.55 and 4.69 (ABq, 2 H, J_{AB} 19.1 Hz, CH_2-Ph), 4.62 (m, 2 H, $J_{1,2}$ 3.5, $J_{3,4}$ ~4.5 Hz, H-2,3), 4.73 (dd, 1 H, $J_{4,5}$ 5.1, $J_{5,6}$ 2.2 Hz, H-5), 4.89 (dd, 1 H, H-4), 5.14 (d, 1 H, H-6), 5.90 (d, 1 H, H-1), and 7.11–7.83 (m, 9 H, aromatic protons).

*Prepared from **1** by reduction with di-isobutyl aluminum hydride, as described previously[1] {82%, $[\alpha]_D^{20}$ +57.5→35° (*c* 1.2, chloroform); lit.[12] 70%, $[\alpha]_D^{20}$ +54° (*c* 1.5, chloroform)}.

Anal. Calc. for $C_{23}H_{26}O_8S$: C, 59.72; H, 5.67; S, 6.93. Found: C, 59.54; H, 5.84; S, 6.99.

*6-O-Benzoyl-1,2-O-isopropylidene-5-O-toluene-*p*-sulphonyl-(6R)-* (**4**) *and -(6S)-α-*D*-gluco-hexodialdo-1,4:6,3-difuranose* (**5**). — Conventional treatment of **2** with benzoyl chloride–pyridine gave a mixture of **4** and **5**. Crystallisation from ethanol yielded **4** (80.5%), m.p. 179–181° (dec.), $[\alpha]_D^{20}$ +118° (*c* 1.2, chloroform), R_F 0.75 (benzene–ethyl acetate, 5:1). N.m.r. data: δ 1.31 and 1.44 (2 s, 6 H, CMe_2), 2.42 (s, 3 H, Me of Ts), 4.51 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.61 (d, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 4.79 (dd, 1 H, $J_{4,5}$ 4.6 Hz, H-4), 4.94 (dd, 1 H, $J_{5,6}$ 3.3 Hz, H-5), 5.82 (d, 1 H, H-1), 6.12 (d, 1 H, H-6), and 7.1–8.0 (m, 9 H, aromatic protons).

Anal. Calc. for $C_{23}H_{24}O_9S$: C, 57.97; H, 5.08; S, 6.73. Found: C, 58.06; H, 5.12; S, 6.66.

Concentration of the foregoing mother-liquor, trituration of the residue with light petroleum, and recrystallisation of the product from ethanol gave **5** (14%), m.p. 149–151°, $[\alpha]_D^{20}$ −23° (*c* 1, chloroform), R_F 0.70 (benzene–ethyl acetate, 5:1). N.m.r. data: δ 1.31 and 1.47 (2 s, 6 H, CMe_2), 2.33 (s, 3 H, Me of Ts), 4.61 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.73 (d, 1 H, $J_{3,4}$ 4.3 Hz, H-3), 4.87 (dd, 1 H, $J_{4,5} = J_{5,6}$ = 4.5 Hz, H-5), 4.98 (dd, 1 H, H-4), 6.01 (d, 1 H, H-1), 6.25 (d, 1 H, H-6), and 7.06–8.04 (m, 9 H, aromatic protons).

Anal. Calc. for $C_{23}H_{24}O_9S$: C, 57.97; H, 5.08; S, 6.73. Found: C, 57.92; H, 5.01; S, 6.59.

*6-O-Acetyl-5-O-benzoyl-1,2-O-isopropylidene-(6S)-β-*L*-ido-hexodialdo-1,4:6,3-difuranose* (**6**). — A mixture of **4** (1.9 g, 4 mmol), Dowex-1 X1 (AcO^-) resin (5 ml), and acetic anhydride (50 ml) was stirred, and boiled under reflux. After 24–30 h, the mixture was cooled, methanol (50 ml) was added, and the mixture was kept at reflux for 1 h. The resin was collected, and washed with hot methanol (2 × 20 ml), and the combined filtrate and washings were concentrated *in vacuo*. A solution of the coloured syrup in ether was filtered through silica gel, washed twice with 10% aqueous sodium carbonate and water, dried (Na_2SO_4), and concentrated. Recrystallisation of the residue from light petroleum yielded **6** (1.1 g, 75.5%), m.p. 101–103°, $[\alpha]_D^{20}$ −27° (*c* 1, chloroform), R_F 0.70 (benzene–ethyl acetate, 10:1). N.m.r. data: δ 1.37 and 1.49 (2 s, 6 H, CMe_2), 2.12 (s, 3 H, Ac), 4.72 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,5}$ 0.8 Hz, H-2), 4.97 (s, 2 H, H-3,4), 5.44 (d, 1 H, H-5), 6.00 (d, 1 H, H-1), 6.31 (s, 1 H, H-6), and 7.33–8.11 (m, 5 H, Bz).

Anal. Calc. for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05. Found: C, 58.76; H, 5.97.

Under similar reaction conditions, **3**, **5**, and methyl 1,2-*O*-benzylidene-5-*O*-toluene-*p*-sulphonyl-(6*S*)-α-D-*gluco*-hexodialdo-1,4-furanose-6,3-furanoside were unchanged.

*1,2-O-Isopropylidene-β-*L*-ido-hexodialdo-1,4:6,3-difuranose* (**7**). — A solution of **6** (4 g, 11 mmol) in methanol (200 ml) containing sodium methoxide (32 mg, 0.6 mmol) was kept at ambient temperature for 1 h. After being stirred with Amberlite IR-120(H^+) resin (5 ml), the mixture was filtered and concentrated, and a solution of the residue in ethyl acetate was decolorised by passage over silica gel. Recrystallisa-

tion from ethyl acetate–light petroleum yielded **7** as a mixture of anomers [*endo*-HO-6(6*R*), *exo*-HO-6(6*S*) ~3:7 (by n.m.r. spectroscopy)] (1.8 g, 75%), m.p. 98–105°, $[\alpha]_D^{20}$ +5° (*c* 1, methanol; no mutarotation), R_F 0.38 (benzene–ethyl acetate, 1:1). N.m.r. data (acetone-d_6 and D_2O): δ 1.37 and 1.51 (2 s, 6 H, CMe_2), 4.01 [d, 0.3 H, $J_{5,6}$ 3.7 Hz, H-5(6*S*)], 4.04 [s, 0.7 H, H-5(6*R*)], 4.42–4.73 (m, 3 H, H-2,3,4), 5.30 [s, 0.7 H, H-6(6*R*)], 5.42 [d, 0.3 H, H-6(6*S*)], 5.84 [d, 0.3 H, $J_{1,2}$ 3.7 Hz, H-1(6*S*)], and 5.91 [d, 0.7 H, $J_{1,2}$ 3.7 Hz, H-1(6*R*)].

Anal. Calc. for $C_9H_{14}O_6$: C, 49.54; H, 6.47. Found: C, 49.62; H, 6.53.

1,2-O-Isopropylidene-β-L-idofuranurono-6,3-lactone (**8**). — A solution of **7** (1 g, 4.6 mmol) in distilled water (500 ml) containing suspended platinum (from 0.3 g of Adams' catalyst) was rapidly stirred and oxygenated at room temperature. After 30–60 min, the solution was filtered and concentrated to a small volume, and the precipitate was collected, and recrystallised from water, to yield **8** (0.7 g, 70%), m.p. 136–136.5°, $[\alpha]_D^{20}$ +102° (*c* 2, acetone), R_F 0.85 (benzene–ethyl acetate, 1:1); lit.[3] m.p. 137–138°, $[\alpha]_D^{20}$ +100° (*c* 2, acetone).

More **8** (0.18 g, 18%) was obtained from the mother liquors.

*6-O-Benzoyl-1,2-O-benzylidene-5-O-toluene-*p*-sulphonyl-(6*R*)-α-*D*-gluco-hexodialdo-1,4:6,3-difuranose* (**12**). — To a stirred solution of **11**[1] (10 g, 24 mmol) and triethylamine (11.6 g, 0.115 mol) in chloroform (100 ml) was slowly added a solution of benzoyl chloride (5 g, 36 mmol) in chloroform (50 ml) at room temperature. After 2 h, methanol (5 ml) was added, stirring was continued for 15 min, and the solution was washed thrice with dilute hydrochloric acid, and then with water, aqueous sodium hydrogen carbonate, and water, and concentrated. Recrystallisation of the brown residue from ethanol–acetone yielded **12** (9.35 g, 75%), m.p. 172–173°, $[\alpha]_D^{20}$ +129° (*c* 1.25, acetone), R_F 0.60 (benzene–ethyl acetate, 10:1). N.m.r. data: δ 2.33 (s, 3 H, Me of Ts), 4.87 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.92 (d, 1 H, $J_{3,4}$ 3.7 Hz, H-3), 5.08 (dd, 1 H, $J_{4,5}$ 4.5 Hz, H-4), 5.15 (dd, 1 H, $J_{5,6}$ 2.5 Hz, H-5), 5.95 (s, 1 H, PhC*H*), 6.16 (d, 1 H, H-1), 6.31 (d, 1 H, H-6), and 7.2–8.0 (m, 14 H, aromatic protons).

Anal. Calc. for $C_{27}H_{24}O_9S$: C, 61.82; H, 4.61; S, 6.11. Found: C, 61.70; H, 4.65; S, 5.97.

The mother liquor contained (t.l.c.) a minor proportion of **12**, together with the (6*S*)-isomer **13** (see below).

*6-O-Benzoyl-1,2-O-benzylidene-5-O-toluene-*p*-sulphonyl-(6*S*)-α-*D*-gluco-hexodialdo-1,4:6,3-difuranose* (**13**). — Benzoyl chloride (5 g, 36 mmol) at 4° was added to a cooled solution of **11** (10 g, 24 mmol) in dry pyridine (120 ml). After 15 min at 0–5°, the mixture was poured into ice–water (700 ml) with vigorous stirring. The product was collected, repeatedly washed with water, dried, and crystallised from ethanol–acetone, to yield **13** (9.2 g, 73%), m.p. 187–188°, $[\alpha]_D^{20}$ −2° (*c* 1.5, acetone), R_F 0.50 (benzene–ethyl acetate, 10:1). N.m.r. data: δ 2.33 (s, 3 H, Me of Ts), 4.78 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.85 (d, 1 H, $J_{3,4}$ 4.5 Hz, H-3), 4.87 (dd, 1 H, $J_{4,5}$ 4.5 Hz, H-5), 5.05 (dd, 1 H, H-4), 5.92 (s, 1 H, PhC*H*), 6.16 (d, 1 H, H-1), 6.32 (d, 1 H, H-6), and 7.2–8.0 (m, 14 H, aromatic protons).

Anal. Calc. for $C_{27}H_{24}O_9S$: C, 61.82; H, 4.61; S, 6.11. Found: C, 61.74; H, 4.68; S, 6.04.

*6-O-Acetyl-5-O-benzoyl-1,2-O-benzylidene-(6S)-β-*L*-ido-hexodialdo-1,4:6,3-difuranose* (**14**). — Treatment of **12**, as described above for **4**, yielded **14** (91%), m.p. 97–98°, $[\alpha]_D^{20}$ −2° (*c* 1.1, acetone), R_F 0.56 (benzene–ethyl acetate, 10:1). N.m.r. data: δ 2.13 (s, 3 H, Ac), 4.92 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 5.00 and 5.12 (ABq, 2 H, J_{AB} 4.5 Hz, H-3,4), 5.49 (s, 1 H, H-5), 5.95 (s, 1 H, PhC*H*), 6.17 (d, 1 H, H-1), 6.35 (s, 1 H, H-6), and 7.33–8.11 (m, 10 H, aromatic protons).

Anal. Calc. for $C_{22}H_{20}O_8$: C, 64.07; H, 4.89. Found: C, 63.95; H, 4.92.

The (6*S*)-anomer **13** was unaffected under the above conditions.

*1,2-O-Benzylidene-β-*L*-ido-hexodialdo-1,4:6,3-difuranose* (**15**). — Deacylation of **14**, as described for **6**, gave **15** (76%), m.p. 147–149.5°, $[\alpha]_D^{20}$ +77° (equil., *c* 1, acetone), R_F 0.75 (benzene–ethyl acetate, 5:1). N.m.r. data (acetone-d_6 and D_2O): δ 4.12 [dd, 0.25 H, $J_{4,5}$ ~1, $J_{5,6}$ 3.7 Hz, H-5(6*S*)], 4.15 [s, 0.75 H, H-5(6*R*)], 4.79 (dd, 1 H, $J_{3,4}$ 4.5 Hz, H-4), 4.89 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-2), 4.90 (d, 1 H, H-3), 5.40 [s, 0.75 H, H-6(6*R*)], 5.42 [d, 0.25 H, H-6(6*S*)], 5.98 [s, 0.75 H, PhC*H*(6*R*)], 6.01 [s, 0.25 H, PhC*H*(6*S*)], 6.03 [d, 0.25 H, H-1(6*S*)], 6.11 [d, 0.75 H, H-1(6*R*)], and 7.45 (m, 5 H, Ph).

Anal. Calc. for $C_{13}H_{14}O_6$: C, 58.64; H, 5.30. Found: C, 58.58; H, 5.31.

*1,2-O-Benzylidene-β-*L*-idofuranurono-6,3-lactone* (**16**). — A solution of **15** (2.0 g, 7.5 mmol) in acetone–water (200 ml, 1:2) was oxidised, as described above for **8**, in the presence of platinum black (from 1 g of platinum oxide). After 8–12 h, when 70–80% of **15** had been oxidised, the catalyst was collected and washed with acetone, and the combined filtrate and washings were concentrated to dryness under reduced pressure. The residue was crystallised from aqueous methanol, to give **16** (1.2 g, 60%), m.p. 168–169°, $[\alpha]_D^{20}$ +92.5° (*c* 2, acetone), R_F 0.86 (benzene–ethyl acetate, 1:1). N.m.r. data (acetone-d_6 and D_2O): δ 4.23 (s, 1 H, H-5), 4.89 (d, 1 H, $J_{3,4}$ 4.5 Hz, H-4), 5.05 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-2), 5.23 (d, 1 H, H-3), 6.15 (s, 1 H, PhC*H*), 6.15 (d, 1 H, H-1), and 7.45 (m, 5 H, Ph).

Anal. Calc. for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found: C, 59.12; H, 4.56.

A second crop (0.2 g, 10%) was obtained from the mother liquor.

L-*Idofuranurono-6,3-lactone* (**9**). — A solution of **16** (0.5 g, 1.9 mmol) in acetic acid (50 ml) was hydrogenated in the presence of palladium-on-charcoal (0.5 g, 5%) for 36 h; no starting material then remained (t.l.c.). Filtration and removal of the solvent under reduced pressure, followed by repeated trituration of the residue with ethyl acetate (200 ml), yielded amorphous **9** (0.23 g, 70%), $[\alpha]_D^{20}$ +68° (*c* 0.85, acetic acid), R_F 0.38 (ethyl acetate). N.m.r. data (D_2O): δ 4.36 (s, 1 H, H-5), 4.46 (s, 1 H, H-2), 4.75 (s, HOD), 4.95 and 5.13 (2 d, 2 H, $J_{3,4}$ 6.0 Hz, H-3,4), 5.43 [s, 0.7 H, H-1(α-L)], and 5.49 [d, 0.3 H, $J_{1,2}$ 4.1 Hz, H-1(β-L)].

Methyl L-*idofuranosidurono-6,3-lactones* (**9a**). — Compound **16** (0.265 g, 1 mmol) was stirred with methanol (10 ml) at 60° in the presence of Amberlite IR-120(H^+) resin (0.25 g) for 5 h. The catalyst was collected and washed with methanol, and the combined filtrate and washings were concentrated to dryness.

Elution of the residue from a column (0.5 × 30 cm) of silica gel with benzene–ethyl acetate (1:1) yielded a syrupy $\alpha\beta$-mixture (7:1) of the methyl glycosides **9a** (0.13 g, 68%), $[\alpha]_D^{20}$ +2° (*c* 3, acetone), R_F 0.42 (benzene–ethyl acetate, 1:1). N.m.r. data (acetone-d_6): δ 3.14 and 3.29 [2 s, 3 H, OMe ($\alpha\beta$ ratio 7:1)], 4.01 (s, 1 H, H-5), 4.08 (s, 1 H, H-2), 4.66 and 4.77 (ABq, 2 H, J_{AB} 5.8 Hz, H-3,4), and 4.76 (s, 1 H, H-1).

1,2-O-Isopropylidene-5-S-(2-mercaptoethyl)-5-thio-β-L-idofuranurono-6,3-lactone (**17**). — To the slurry[9] formed by adding 1,2-ethanedithiol (0.29 g, 3.3 mmol) to a solution of trimethyl aluminum (7 mmol) in toluene (4.4 ml), after dilution with dichloromethane (5 ml), was slowly added a solution of **1** (1.17 g, 3 mmol) in dichloromethane (10 ml) with stirring and cooling (−78°). When the reaction mixture had reached ambient temperature, no starting material could be detected (t.l.c.). The solvent was evaporated, and ether (60 ml) and sodium sulphate decahydrate were added to effect slow hydrolysis. The mixture was filtered and concentrated, and the residue was recrystallised from methanol–water, to give **17** (0.42 g, 46%), m.p. 103–104°, $[\alpha]_D^{20}$ +169° (*c* 2, chloroform), R_F 0.57 (benzene–ethyl acetate, 5:1). N.m.r. data: δ 1.34 and 1.51 (2 s, 6 H, CMe_2), 1.56–1.78 (m, 1 H, SH), 2.62–3.22 (m, 4 H, S-CH_2-CH_2-S), 3.64 (s, 1 H, H-5), 4.68 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 4.82 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-2), 4.96 (d, 1 H, H-3), and 5.95 (d, 1 H, H-1).

Anal. Calc. for $C_{11}H_{16}O_5S_2$: C, 45.19; H, 5.52; S, 21.93. Found: C, 45.28; H, 5.44; S, 21.94.

ACKNOWLEDGMENT

This work was supported by a grant from the Fonds zur Förderung der wissenschaftlichen Forschung (Nr. 2290 and 3471).

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