Carbohydrate Research, 205 (1990) 203–210
Elsevier Science Publishers B.V., Amsterdam

Synthesis and reactions of chlorodeoxy-L-talofuranoid derivatives*†

Cheang-Kuan Lee
Department of Chemistry, National University of Singapore, Kent Ridge, 0511 (Singapore)

(Received December 29th, 1989; accepted for publication, February 15th, 1990)

ABSTRACT

Reaction of 6-*O*-acyl-3,5-*O*-benzylidene derivatives of 1,2-*O*-isopropylidene-α-D-glucofuranose with *N*-bromosuccinimide affords mainly 5-*O*-acyl-6-bromo-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose in good yield. Convenient preparative routes to 1,2-*O*-isopropylidene-β-L-talofuranose and its conversion into 5-chloro-5-deoxy and 5,6-dichloro-5,6-dideoxy derivatives are described.

INTRODUCTION

Interest in chlorodeoxy derivatives of sugar arose from the discovery by Hough and his co-workers[2] that the introduction of halogen substituents at certain positions of the sucrose molecule can increase the sweetness of the compound several hundred times. In fact, a group of mixed deoxyhalo derivatives of sucrose was found[3,4] to possess sweetness up to 7500 times that of sucrose.

Systematic studies of the structural and mechanistic aspects associated with sweetness of sugars had been confined mainly to D sugars and their derivatives[4], with only one systematic study[5] being reported for L sugars. Sweeteners derived from L sugars could have considerable advantages, particularly since they are not metabolised and would, therefore, be non-caloric. The synthesis and reactions of chlorodeoxy-1,2-*O*-isopropylidene-β-L-talofuranose derivatives are, therefore, of interest and are now described.

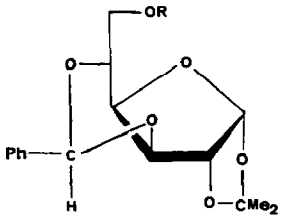
RESULTS AND DISCUSSION

The reaction of benzylidene acetals of sugars with *N*-bromosuccinimide can result[6] in the opening of the acetal ring accompanied by rearrangement leading to the incorporation of bromine at a carbon atom other than those involved in the acetal ring, particularly when nearby participating function(s) are present. Hanessian and Plessas[6] reported that 3,5-*O*-benzylidene-α-D-glucofuranose (**1**) gave mainly 5-*O*-benzoyl-6-bromo-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose together with some 3,6-anhydro-5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose. However, the reaction of

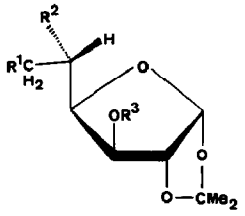
* Dedicated to Professor Leslie Hough in the year of his 65th birthday.
† Chorodeoxy-L-hexofuranoid Derivatives, Part 2. For Part 1, see ref. 1.

0008-6215/90/$ 03.50

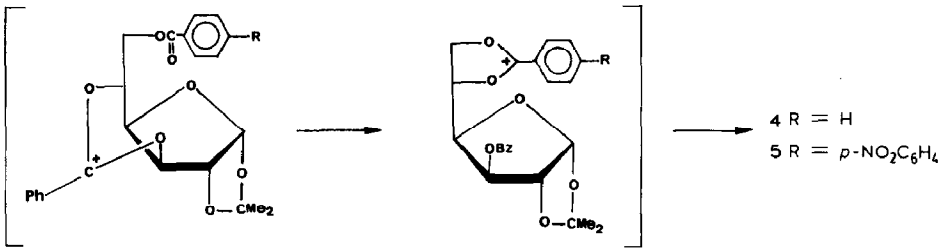
N-bromosuccinimide with the 6-*O*-benzoyl (**2**) or 6-*O*-*p*-nitrobenzoyl[7] (**3**) derivatives of **1** afforded mainly 3,5-di-*O*-benzoyl (**4**) or 3-*O*-benzoyl-5-*O*-*p*-nitrobenzoyl (**5**) derivatives of 6-bromo-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose, respectively. The presence of a bromine substituent in **4** and **5** was evident from their mass spectra. Accurate mass measurement revealed the $[M^+ - 15]$ fragment for **4** at (*m/z* 475:477 (ratio 1:1), and for **5** at *m/z* 520:522 (ratio 1:1). The ^{13}C-n.m.r. spectra clearly showed that the C-6 resonance had been shifted upfield (δ 30.55), due to the shielding effect of the bromine substituent. The L-*ido* configuration of **4** and **5** was confirmed by their conversion into the known crystalline 1,2-*O*-isopropylidene-β-L-idofuranose (**6**) (by reacting **4** and **5**, initially with potassium acetate or benzoate in boiling acetonitrile, to give **7** and **8**, respectively, followed by Zemplén deacylation) and its triacetate[1]. Although there are other mechanistic possibilities, it seems likely that the reaction occurred *via* the benzoxonium ions **9** (Scheme 1).



1 R = H
2 R = Bz
3 R = *p*-$NO_2C_6H_4$



4 R^1 = Br, R^2 = OBz, R^3 = Bz
5 R^1 = Br, R^2 = *p*-$NO_2C_6H_4$, R^3 = Bz
6 R^1 = R^2 = OH, R^3 = H
7 R^1 = OAc, R^2 = *p*-$NO_2C_6H_4$, R^3 = Bz
8 R^1 = R^2 = OBz, R^3 = Bz



9

4 R = H
5 R = *p*-$NO_2C_6H_4$

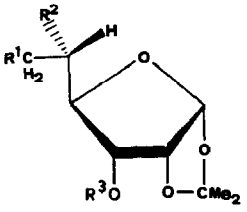
Scheme 1

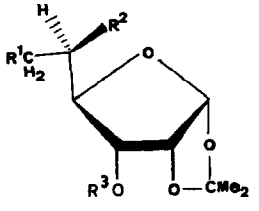
The necessary L-talose precursor (**10**) was obtained from 1,2-*O*-isopropylidene-β-L-idofuranose (**6**) by isopropylidenation in acetone–2,2-dimethoxypropane[8] and epimerisation at C-3 by an oxidation–reduction sequence, to give the known 1,2:5,6-di-*O*-isopropylidene-β-L-talofuranose[9], mild acid hydrolysis of which gave **10** in ~52% overall yield.

Compound **10** was also prepared by the reaction under nitrogen of 3-*O*-benzoyl-1,2-*O*-isopropylidene-5,6-di-*O*-mesyl-α-D-allofuranose[9] (**11**) with potassium acetate or benzoate in *N*,*N*-dimethylformamide at ~90° for 8–10 h in the presence of

18-Crown-6, to give **14** and **15**, respectively, in yields of 71–78%. Deacylation with methanolic sodium methoxide then gave **10**.

The initial displacement of MsO-6 of **11** by acetate or benzoate to give **12** or **13** (~83%), respectively, was readily effected[1] in boiling acetonitrile in the presence of 18-Crown-6 under nitrogen. No displacement of MsO-5 was observed even after reaction for 24 h. This route provides a convenient synthesis of C-5 derivatives. Thus, 6-*O*-acetyl-3-*O*-benzoyl-5-chloro-5-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose (**16**) was obtained in ~80% yield when **12** was treated with potassium chloride in *N,N*-dimethylformamide. The mass spectrum of **16** clearly reflected a chloro substituent, as indicated by the $[M^+ - 15]$ fragment at *m/z* 369 (ratio 3:1) in the mass spectrum. Also, in the ^{13}C-n.m.r. of **16**, the C-5 resonance (δ 57.5) was shifted upfield by ~15 p.p.m. compared to those for **12**, **13**, and **17**.





10 $R^1 = R^2 = OH, R^3 = H$
14 $R^1 = R^2 = OAc, R^3 = Bz$
15 $R^1 = R^2 = OBz, R^3 = Bz$
16 $R^1 = OAc, R^2 = Cl, R^3 = Bz$
20 $R^1 = Cl, R^2 = OH, R^3 = H$
21 $R^1 = R^2 = Cl, R^3 = Bz$

11 $R^1 = R^2 = OMs, R^3 = Bz$
12 $R^1 = OAc, R^2 = OMs, R^3 = Bz$
13 $R^1 = OBz, R^2 = OMs, R^3 = Bz$
17 $R^1 = R^2 = OH, R^3 = H$
18 $R^1 = R^2 = Cl, R^3 = H$
19 $R^1 = R^2 = Cl, R^3 = Ac$

The reaction of **10** with sulphuryl chloride (3 equiv.), initially at ~ −55° and then at ~ −10° for 12 h, gave, after dechlorosulphation, two major faster-moving components which were isolated by flash chromatography and shown to be 5,6-dichloro-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-allofuranose (**18**, 36%) (by conversion into its 3-acetate **19**) and 6-chloro-6-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose (**20**, 26%). Compound **20** could be obtained in ~65% yield by carrying out the reaction using 1.2 equiv. of sulphuryl chloride at ~ −30° for ~15 h. Likewise, the yield of **18** was increased to ~63% when the reaction mixture was stirred at room temperature for ~10 h.

The presence of chlorine substituent(s) in derivatives **18** and **20** was confirmed from the n.m.r. and mass-spectral data. Accurate mass measurement showed a fragment ion $[M^+ - 15]$ at *m/z* 223 for **20**, corresponding to $C_8H_{12}ClO_5$ (ratio 3:1) and *m/z* 242 for **18**, corresponding to $C_8H_{11}Cl_2O_4$ (ratio 9:6:1). The resonances due to H-3,4,5 in the ^1H-n.m.r. spectrum of **20** overlapped, but the spectrum of the trichloroacetylcarbamate derived from **20** contained two high-field NH singlets and, although the signals due to H-3 and H-5 were still unresolved, they had been deshielded by ~0.1 p.p.m., thereby indicating the position of the hydroxyl groups in **20**. Furthermore, the ^{13}C-n.m.r. spectrum of **19** showed an upfield shift of the resonance for C-6 by ~19 p.p.m.

TABLE I

^{1}H-N.m.r. (90 MHz) data[a] for solutions in deuteriochloroform

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*CMe_2*	*Other signals*
4	6.04(d)	4.67(d)	5.60(d)	4.87(dd)	5.5–5.7(m)	4.6–4.8(m)	3.65(dd)	1.59, 1.32	
5	6.05(d)	4.69(d)	5.63(d)	4.85(dd)	5.6–5.7(m)	3.74(dd)	3.58(dd)	1.62, 1.36	
7	6.05(d)	4.71(d)	5.60(d)	4.73(dd)	5.8–5.9(m)	4.57(dd)	4.28(dd)	1.59, 1.34	1.99(MeCO)
8	6.07(d)	4.69(d)	5.61(d)	4.82(dd)	5.8–6.0(m)	4.76(dd)	4.50(dd)	1.59, 1.34	
12	5.89(d)	–0.0-0.0–5.0–5.3(m)		4.52(dd)	5.0–5.3(m)	4.53(dd)	4.18(dd)	1.54, 1.33	2.05(MeCO) 3.05($MeSO_2$)
13	5.91(d)	5.1–5.4(m)		4.57(dd)	5.1–5.4(m)	4.73(dd)	4.54(dd)	1.55, 1.33	3.04($MeSO_2$)
14	5.90(d)	4.95(dd)	4.88(t)	4.43(dd)	5.33(m)	4.67(dd)	4.21(dd)	1.57, 1.34	2.01, 2.04(MeCO)
15	5.96(d)	5.0–5.1(m)			5.80(m)	4.6–4.8(m)		1.57, 1.34	
16	5.94(d)	4.98(dd)	5.19(dd)	4.56(dd)		4.1–4.5(m)		1.55, 1.35	2.09(MeCO)
19	5.83(d)	4.83(dd)	4.95(dd)	4.51(dd)	4.20(dd)	3.64(d)		1.56, 1.35	2.15(MeCO)
20	5.83(d)	4.60(dd)			3.4–4.0(m)		–0.0-0.0–	1.58, 1.38	2.41, 2.51(OH)
20[b]	5.90(d)	4.8–5.0(m)		4.4–4.6(m)	5.24(td)	3.80(d)		1.58, 1.37	8.65(NH)
21	5.93(d)	4.99(dd)	5.19(dd)	4.80(dd)	4.24(td)	3.92(dd)	3.84(dd)	1.56, 1.35	

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
4	3.8	0	3.4	7.1	3.7	4.7	6.6
5	3.7	0	3.0	7.0	4.5	5.0	12.0
7	3.7	0	3.0	7.0	4.0	5.5	12.2
8	3.7	0	3.2	7.3	3.9	5.6	12.2
12	3.7	0	3.4	9.3	3.3	7.7	12.2
13	3.4	0	3.5	7.6	3.6	4.9	12.2
14	3.7	4.6	4.6	3.4	3.6	7.3	12.4
15	3.4						
16	3.6	4.8	8.3	2.1			
19	3.4	5.3	7.7	5.3	6.5		
20	3.7	4.7					
20[b]	3.4			3.7	5.6		
21	3.7	4.7	8.1	1.7	7.5	6.9	2.7

[a] Chemical shifts in p.p.m., J in Hz. [b] With trichloroacetyl isocyanate.

TABLE II

^{13}C-Chemical shifts[a] for solutions in $CDCl_3$

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	CMe_2	CMe_2	*COMe*	$MeSO_2$
4	104.7	83.6	80.1	76.7	70.4	30.6	112.5	26.8, 26.3		
5	104.7	83.7	78.4	76.5	71.5	30.3	112.7	26.8, 26.3		
7	104.5	83.5	77.4	76.4	70.7	62.4	112.4	26.6, 26.0	20.4	
8	104.7	83.2	77.5	77.0	69.9	63.4	112.5	26.8, 26.3		
12	104.2	77.8/77.4		76.3	72.5	61.9	113.5	26.5, 26.5	20.7	38.5
13	104.3	77.8/77.5		76.5	72.6	62.6	113.6	26.7, 26.7		38.7
14	104.3	77.3/76.2		72.2	68.8	62.8	113.4	26.6, 26.6	20.7, 20.6	
15	104.5	77.4/76.5		72.6	69.6	63.5	113.4	26.7, 26.7		
16	104.8	77.6/77.5		73.7	57.5	65.1	113.6	26.8, 26.8	20.7	
19	104.1	77.8/77.4		73.4	60.4	45.1	113.5	26.7, 26.7	20.6	
20	104.2	79.9/78.7		71.6	70.2	46.0	113.1	26.6, 26.6		
21	104.8	77.9/76.6		73.8	59.7	44.4	113.8	26.8, 26.8		

[a] P.p.m. downfield from DSS.

with respect to those for **10** and **17**. Likewise, the ^{13}C-n.m.r. spectrum of **18** showed upfield shifts of the resonances of C-5 and C-6 by ~10 and ~20 p.p.m., respectively, with respect to those for **10** and **17**, clearly indicating the positions of the chloro substituents in **18**.

Similar treatment of 3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-allofuranose with sulphuryl chloride yielded, as expected, 3-*O*-benzoyl-5,6-dichloro-5,6-dideoxy-β-L-talofuranose (**21**). The presence of chloro substituents at C-5 and C-6 was evident from the n.m.r. and mass-spectral data (Tables I and II).

EXPERIMENTAL

For general experimental details, see ref. 1

3,5-Di-O-benzoyl-6-bromo-6-deoxy-1,2-O-isopropylidene-β-D-idofuranose (**4**). — To a solution of **2** (2.1 g) in carbon tetrachloride (50 mL) were added recrystallised *N*-bromosuccinimide (1.0 g) and barium carbonate (3.0 g). The mixture was boiled under reflux for 2.5 h, when t.l.c. (ethyl acetate–hexane, 3:1) showed major and minor fast-moving spots with similar R_F values. The suspension was filtered and concentrated. Flash chromatography (ethyl acetate–hexane, 3:1) of the residue gave **4** (1.8 g, 84%), isolated as a syrup, $[\alpha]_D$ −6° (*c* 0.45, chloroform) (Found: C, 56.3; H, 4.6; Br, 16.2. $C_{23}H_{23}BrO_7$ calc.: C, 56.3; H, 4.7; Br, 16.1%).

3-O-Benzoyl-6-bromo-6-deoxy-1,2-O-isopropylidene-5-O-p-nitrobenzoyl-β-L-idofuranose[7] (**5**). — Compound **3** was treated with *N*-bromosuccinimide as for **4**, to yield **5** (1.4 g, 75%), $[\alpha]_D$ −47° (*c* 0.5, acetone) (Found: C, 51.2; H, 4.45; Br, 15.2; N, 2.9. $C_{23}H_{22}BrNO_9$ calc.: C, 51.6; H, 4.1; Br, 14.8; N, 2.6%).

3,5,6-Tri-O-benzoyl-1,2-O-isopropylidene-β-L-idofuranose (**8**). — Acetonitrile (15 mL) containing activated alumina (0.5 g) was stirred with potassium benzoate (0.75 g) for 15 min. 18-Crown-6 (0.1 g) was added, followed by **4** (0.63 g), and the mixture was boiled under reflux for 6 h under nitrogen. T.l.c. (ethyl acetate–hexane, 3:1) then showed only one fast-moving spot. The mixture was filtered and concentrated, and the syrupy residue was eluted from a short column of silica gel, with the above solvent, to yield **8** (76.5%), m.p. 102–104°, $[\alpha]_D$ −9° (*c* 0.4, acetone) (Found; 67.3; H, 5.0. $C_{30}H_{28}O_9$ calc.: C, 67.7; H, 5.3%).

6-O-Acetyl-3-O-benzoyl-1,2-O-isopropylidene-5-O-p-nitrobenzoyl-β-L-idofuranose (**7**). — Compound **5** was treated with potassium acetate as above to yield syrupy **7** (72.3%), $[\alpha]_D$ +4° (*c* 0.4, chloroform) (Found: C, 58.3; H, 5.1; N, 2.55. $C_{25}H_{25}NO_{11}$ calc.: 58.25; H, 4.85; N, 2.7%).

1,2-O-Isopropylidene-β-L-idofuranose (**6**). — Compounds **7** and **8** were each deacylated with methanolic 0.1M sodium methoxide for 1 h at room temperature. Each solution was deionised with Duolite MB 5113 mixed-bed resin and concentrated to give **6**, m.p. 111–114° (from ether), $[\alpha]_D$ −20° (*c* 0.55, methanol); lit.[8] m.p. 112–113°, $[\alpha]_D$ −19° (methanol).

1,2-O-Isopropylidene-β-L-talofuranose (**10**). — (*a*) Compound **6** was converted into 1,2:5,6-di-*O*-isopropylidene-β-L-idofuranose, using acetone–2,2-dimethoxypro-

pane[8]; the diacetal had m.p. 152–154°, $[\alpha]_D$ −20° (*c* 0.5, methanol); lit.[8] m.p. 150–152°, $[\alpha]_D$ −19° (water). A solution of the diacetal (5 g) in methyl sulphoxide (5 mL) and *N,N*-dimethylformamide (32 mL) was heated with phosphorus pentaoxide (5.0 g) at 65° for 2.5 h, when t.l.c. showed that the reaction was complete. The mixture was poured into vigorously stirred ice–water, the precipitate was collected, and a solution in methanol (20 mL) was treated with sodium borohydride (1.0 g) during 0.5 h. The solution was stirred at room temperature for 1.5 h, then neutralised with Duolite mixed-bed resin, and concentrated to dryness. A solution of the syrupy residue in methanol (10 mL) and aqueous 0.8% sulphuric acid (10 mL) was stirred at room temperature for 2.5 h, when t.l.c. (ethyl acetate–hexane, 3:1) showed one major and a minor product. The solution was neutralised ($BaCO_3$), filtered, and concentrated to give **10** (2.6 g, 52%), m.p. 91–93°, $[\alpha]_D$ +52° (*c* 0.5, ethanol); lit.[9] m.p. 100–101°, $[\alpha]_D$ +52° (methanol).

(*b*) A solution of 3-*O*-benzoyl-1,2-*O*-isopropylidene-5,6-di-*O*-mesyl-α-D-allofuranose[8] (**11**, 3.0 g) in *N,N*-dimethylformamide (15 mL) was treated with potassium acetate (3.0 g) as described for **8**. After ~8 h at ~90°, t.l.c. revealed one fast-moving and several slower minor components. Work-up in the usual manner afforded 5,6-di-*O*-acetyl-3-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-talofuranose (**14**, 77.7%), m.p. 69–71°, $[\alpha]_D$ +72° (*c* 0.8, acetone) (Found: C, 58.8, H, 5.7. $C_{20}H_{24}O_9$ calc.: C, 58.9; H, 5.9%).

A solution of **11** (3.5 g) was treated similarly with potassium benzoate (3.5 g), as described above, to give 3,5,6-tri-*O*-benzoyl-1,2-*O*-isopropylidene-β-L-talofuranose (**15**, 71.2%), m.p. 147–148° (from ethanol), $[\alpha]_D$ +88° (*c* 0.7, acetone); lit.[9] m.p. 156–158°, $[\alpha]_D$ +90° (chloroform).

A solution of **14** and **15** in methanol was treated with a catalytic amount of sodium methoxide for 0.5 h at room temperature. The solution was deionised with Duolite MB 5113 mixed-bed resin and concentrated to give a product identical to that obtained in (*a*).

6-O-Acetyl-3-O-benzoyl-1,2-O-isopropylidene-5-O-mesyl-α-D-allofuranose (**12**). — Reaction of **11** with potassium acetate, as described for **8**, gave, after 3 h at 70°, **12** (82.9%), m.p. 78–80°, $[\alpha]_D$ +101.8° (*c* 0.6, acetone) (Found: C, 50.8; H, 5.2; S, 7.4. $C_{19}H_{24}O_{10}S$ calc.: C, 51.35; H, 5.4; S, 7.2%).

3,6-Di-O-benzoyl-1,2-O-isopropylidene-5-O-mesyl-α-D-allofuranose (**13**). — Reaction of **11** was repeated with potassium benzoate, with boiling under reflux for 6 h, to yield **13** (89.4%), m.p. 128–129° (from ethanol), $[\alpha]_D$ +91° (*c* 0.3, ethanol) (Found: C, 57.2; H, 5.4; S, 6.0. $C_{24}H_{26}O_{10}S$ calc.: C, 56.9; H, 5.1; S, 6.3%).

6-O-Acetyl-3-O-benzoyl-5-chloro-5-deoxy-1,2-O-isopropylidene-β-L-talofuranose (**16**). — Reaction of **12** with potassium chloride in *N,N*-dimethylformamide, as described for **8**, gave, after 8 h, syrupy **16** (80%), $[\alpha]_D$ +66° (*c* 0.8, acetone) (Found: C, 56.5; H, 5.6; Cl, 9.5. $C_{18}H_{21}ClO_7$ calc.: C, 56.2; H, 5.5; Cl, 9.2%).

Reaction of sulphuryl chloride with 1,2-O-isopropylidene-β-L-talofuranose (**10**). — To a solution of **10** (1.6 g) in pyridine (6 mL) and chloroform (6 mL) at ~ −50° was added a solution of sulphuryl chloride (2 mL) in chloroform (2 mL) dropwise during 15 min. The mixture was kept overnight at ~ −10°, when t.l.c. (ethyl acetate–hexane, 1:1)

revealed two major and several minor fast-moving products. The mixture was poured into vigorously stirred, ice-cold, aqueous 10% sulphuric acid (20 mL) and extracted with dichloromethane (2 × 10 mL). The combined extracts were washed successively with water, saturated aqueous sodium hydrogencarbonate, and water, then concentrated. A solution of the syrupy residue in methanol (10 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. Flash chromatography (ethyl acetate–hexane, 1:1) of the residue gave, first, 5,6-dichloro-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-allopyranose (**18**, 38%), $[\alpha]_D$ +49° (*c* 0.25 methanol) (Found: C, 41.8; H, 5.7; Cl, 28.0 $C_9H_{14}Cl_2O_4$ calc.: C, 42.0; H, 5.4; Cl, 27.6%).

Eluted second was 6-chloro-6-deoxy-1,2-*O*-isopropylidene-β-L-talofuranose (**20**, 26%), m.p. 146–148°, $[\alpha]_D$ +74° (*c* 0.15, ethanol) (Found: C, 45.0; H, 6.0; Cl, 15.2. $C_9H_{15}ClO_5$ calc.: C, 45.3; H, 6.3; Cl, 14.9%).

When the reaction was carried out as above but left for ~10 h at room temperature, one major and traces of several fast-moving products were formed and ~63% of **18** was isolated.

When the reaction was repeated with 1.2 equiv. of sulphuryl chloride and the mixture was worked-up after ~10 h at ~ −30°, ~65% of **20** was obtained.

3-O-Acetyl-5,6-dichloro-5,6-dideoxy-1,2-O-isopropylidene-α-D-allofuranose (**19**). — Conventional acetylation of **18** in pyridine and acetic anhydride gave **19** (89%), $[\alpha]_D$ +96° (*c* 0.25, acetone) (Found: C, 44.7; H, 5.7; Cl, 24.0. $C_9H_{14}Cl_2O_4$ calc.: C, 44.15; H, 5.35; Cl, 23.75%).

3-O-Benzoyl-5,6-dichloro-5,6-dideoxy-1,2-O-isopropylidene-β-L-talofuranose (**21**). — Treatment of 3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-allofuranose[9] with sulphuryl chloride (2.5 equiv.), as described for **18**, gave **21** as a syrup (58.4%), $[\alpha]_D$ +109° (*c* 0.5, acetone) (Found; C, 53.8; H, 5.1; Cl, 19.7. $C_{16}H_{18}Cl_2O_5$ calc.: C, 53.2; H, 5.0; Cl, 19.7%).

ACKNOWLEDGMENTS

The Shaw Foundation is thanked for financial support, and Ms. S. Y. Wong, Ms. L. K. Wong, and Mr. B. H. Yeo are thanked for help with recording the ^{1}H- and ^{13}C-n.m.r. and mass spectra.

REFERENCES

1 C. K. Lee, *Carbohydr. Res.*, 177 (1988) 247–252.
2 L. Hough and S. Phadnis, *Nature (London)*, 263 (1976) 800–802; L. Hough and R. Khan, *Trends. Biochem. Sci.*, (1978) 61–63.
3 C. K. Lee, Br. Pat. 2,088,885A (1982); *Chem. Abstr.*, 97 (1982) 145225q; U.S. Pat. 4,405,654 (1983); *Chem. Abstr.*, 100 (1984) 33495b.
4 C. K. Lee. *Adv. Carbohydr. Chem. Biochem.*, 45 (1984) 199–351.
5 R. S. Shallenberger, T. E. Acree, and C. Y. Lee, *Nature (London)*, 221 (1969) 555–556.
6 J. W. Van Cleve, G. E. Inglett, and L. W. Tjarks, *Carbohydr. Res.*, 137 (1985) 259–264.
7 S. Hanessian and N. R. Plessas, *J. Org. Chem.*, 34 (1969) 1053–1058.
8 N. A. Hughes and N. M. Munkombwe, *Carbohydr. Res.*, 101 (1982) 221–229.
9 T. Naka, T. Hashizume, and M. Nishimura, *Tetrahedron Lett.*, (1971) 95–98.