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α-D-ALLOPYRANOSYL β-D-FRUCTOFURANOSIDE (*allo*-SUCROSE) AND ITS DERIVATIVES*

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ABSTRACT

Reduction of 3-ketosucrose (**1**) with sodium borohydride gave mainly α-D-allopyranosyl β-D-fructofuranoside (**2**), characterised as its octabenzoate. Using sodium borodeuteride, [3-^{2}H]*allo*-sucrose (**5**) and [3-^{2}H]sucrose (**6**) were obtained in the ratio 12:1. The mixture was fractionated on Dowex-50 X8 resin (Ca^{2+} form), and the [3-^{2}H] derivatives were isolated as their octa-acetates. Inspection of the ^{13}C-n.m.r. spectra of **5** and **6** enabled the C-3 signals to be assigned. *allo*-Sucrose (**2**) was more readily obtained by oxidation of sucrose with dimethyl sulphoxide–acetic anhydride followed by reduction with sodium borohydride and fractionation on Dowex-50 X8 (Ca^{2+}) resin. Tritylation of **2** followed by acetylation gave, after chromatography, the 6,1′,6′-tritrityl ether (**9**, 10%), the 6,6′-ditrityl ether (**10**, 26%), and a mixture of monotrityl ethers (20%). Hydrogenolysis of **9** and **10** gave the penta-acetate and hexa-acetate, respectively, with no detectable migration of AcO-4. Treatment of **2** with sulphuryl chloride at −50° gave the 6,6′-dichloride.

INTRODUCTION

In exploring the chemistry of sucrose, we have investigated the synthesis and properties of *allo*-sucrose (**2**) and its derivatives. Compound **2** was first synthesised[1] in low yield by the reduction of β-D-fructofuranosyl α-D-*ribo*-hexopyranosid-3-ulose (3-ketosucrose; **1**), the product of oxidation of sucrose by *Agrobacterium tumefaciens*, but was not rigorously characterised.

RESULTS

3-Ketosucrose (**1**) was isolated from a clarified concentrate of the culture medium of *A. tumefaciens* by fractionation on a short column of charcoal[2]. Re-

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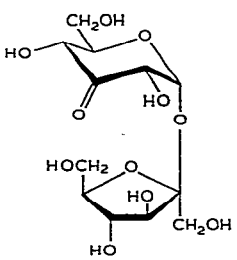
TABLE I

^{1}H-N.M.R. PARAMETERS[a]: FIRST-ORDER CHEMICAL SHIFTS (τ) AND COUPLING CONSTANTS (Hz) AT 220 MHz

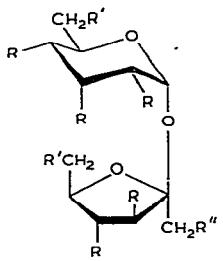
	3[b]	4[d]	7[b]	8[b]	9[c]	10[c]	13[c]	14[b]	15[b]
H-1	4.24d	3.6d	4.13d	4.27d	4.75d	4.45d	4.44d	4.5d	4.35d
H-2	5.17t	4.4t	4.99d	5.22d	5.17t	5.07t	5.07t	5.28t	5.29t
H-3	4.1t	3.71t	—	—	4.53t	4.41t	4.37t	4.12t	4.13t
H-4	4.89q	4.29q	4.69d	4.93d	4.87q	4.80q	5.1q	4.98q	5.03q
H-3′	4.29d	3.70d	4.3d	4.29d	4.28d	4.7d	4.52d	4.1d	4.29d
H-4′	4.42t	3.58t	4.46t	4.42t	4.63t	4.51t	4.60t	4.35t	4.43t
OAc	8.01–8.31		8.13–8.39	8.03–8.34	8.06–8.39	7.91–8.28	7.87–7.98	8.14–8.4	8.15–8.4
OTr					2.06–2.4	2.6–2.85			
OMs							6.93s		
OBz		1.9–2.8							
$J_{1,2}$	4.5	4.0	4.0	4.5	4.5	4.0	4.5	4.5	4.5
$J_{2,3}$	3.5	3.5	—	—	3.0	3.0	3.0	3.5	3.5
$J_{3,4}$	3.5	3.5	—	—	3.0	3.0	3.0	3.5	3.0
$J_{4,5}$	10.5	10.5	10.0	10.0	10.5	11.0	10.5	10.0	10.5
$J_{3',4'}$	6.0	7.5	5.5	6.0	7.0	7.0	7.0	6.5	6.0
$J_{4',5'}$	6.0	7.5	5.5	6.0	7.0	7.0	7.0	6.5	6.0

[a]Key: s, singlet; d, doublet; t, triplet; q, quartet. The resonances due to H-5, H-5′, H-6, and H-6′ appeared as complex, overlapped multiplets in the region τ 5.1–6.0. [b]In C_6D_6. [c]In $CDCl_3$. [d]In CD_3COCD_3.

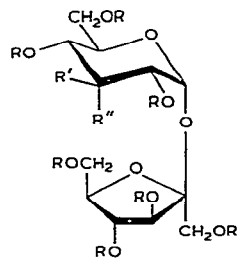
duction of **1** with aqueous sodium borohydride gave, as expected, mainly the axial 3-ol, *allo*-sucrose (**2**), which was isolated *via* its octa-acetate (**3**). The structure of **2** was deduced by acid hydrolysis, which gave allose and fructose (as determined by automated ion-exchange chromatography[3]), and by the ^{1}H-n.m.r. spectrum of **3** (Table I), which showed the anticipated signals for an α-D-allopyranosyl residue with $J_{1,2}$ 4.5, $J_{2,3}$ 3.5, $J_{3,4}$ 3.5, and $J_{4,5}$ 10.5 Hz. The crystalline octabenzoate **4** was used for the characterisation of **2**.



1



2 R = R′ = R″ = OH
3 R = R′ = R″ = OAc
4 R = R′ = R″ = OBz
9 R = OAc, R′ = R″ = OTr
10 R = R″ = OAc, R′ = OTr
11 R = OH, R′ = R″ = OTr
12 R = R″ = OAc, R′ = OH
13 R = R″ = OAc, R′ = OMs
14 R = OAc, R′ = R″ = Cl
15 R = R″ = OAc, R′ = Cl



5 R = H, R′ = ^{2}H, R″ = OH
6 R = H, R′ = OH, R″ = ^{2}H
7 R = Ac, R′ = OAc, R″ = ^{2}H
8 R = Ac, R′ = ^{2}H, R″ = OAc

Considerable difficulties were originally encountered at M.R.E. (Porton) with the microbiological production of **1**, and consequently a direct chemical synthesis from sucrose was explored, incorporating reduction *in situ* to *allo*-sucrose (**2**).

Lindberg and Slessor[4] observed the formation of **1**, albeit in low yield, when sucrose was oxidised with dimethyl sulphoxide–acetic anhydride. We repeated this oxidation, and then reduced an aqueous solution of the crude product with an excess of sodium borohydride, to give a mixture of sucrose and *allo*-sucrose (**2**) in the ratio of 17:4, as revealed by auto-analysis[3]. Alkaline-earth metal ions complex with three contiguous hydroxyl groups in an axial–equatorial–axial conformation on a pyranoid ring[5], and hence α-D-allopyranosides complex with calcium ions through HO-1,2,3. Consequently, *allo*-sucrose (**2**), but not sucrose, should be retained by the Ca^{2+} form of an ion-exchange resin. When the foregoing mixture was fractionated on Dowex-50 (Ca^{2+}) resin, **2** was isolated in 5% overall yield and characterised as the octabenzoate **4**. It is of interest to note that, whereas 3-ketosucrose (**1**) is similar in sweetness to sucrose, *allo*-sucrose (**2**) is tasteless.

The structure of 3-ketosucrose was confirmed by reduction with sodium borodeuteride, which gave [3-^{2}H]*allo*-sucrose (**5**) and [3-^{2}H]sucrose (**6**) in the ratio 12:1. The deuterated derivatives were isolated by fractionation on Dowex-50 X8 (Ca^{2+}) resin. Elution with water gave initially the sucrose fraction, from which [3-^{2}H]sucrose octa-acetate (**7**) was obtained. [3-^{2}H]*allo*-Sucrose was eluted second and isolated as its octa-acetate (**8**). The 220-MHz, ^{1}H-n.m.r. spectra of **7** and **8** contained no signals for H-3, and the H-2 signals were doublets with $J_{1,2}$ 5.0 Hz. The replacement of a proton by a deuteron has proved useful in signal assignments in ^{13}C-n.m.r. studies[6], the signal of the attached ^{13}C-nucleus either disappearing[7] or being converted into a triplet[8] at 0.1–0.5 p.p.m. to higher field[9–12]. The ^{13}C-chemical shifts of **2**, **3**, **5**, and **8** are listed in Table II (downfield from Me_4Si). The lowest-field resonances (168–170 p.p.m.) were those due to the acetoxyl-carbonyl carbons. The spectra of **2** and **5** were identical, apart from the absence of the C-3 signal at 72.0 p.p.m. in **5**, thus establishing the assignment of the C-3 signal in **2**. Gorin[6] located the C-3 signal for α-D-allopyranose at 72.26 p.p.m., and the other allopyranosyl assignments were in close agreement, apart from that for C-5 which showed a downfield shift of 1.1 p.p.m. For the octa-acetate **3**, the signal at 67.15 p.p.m. was assigned to C-3, since the ^{2}H-analogue **8** lacked this signal. Assignments in the ^{13}C-n.m.r. spectrum of sucrose have been made previously[13,19] and our results are in general agreement with those of Pfeffer *et al.*[13c].

Tritylation of *allo*-sucrose (**2**) with three equivalents of reagent in pyridine and subsequent acetylation gave a mixture which, after fractionation on a column of silica gel, yielded 6,1′,6′-tri-*O*-trityl-*allo*-sucrose penta-acetate (**9**), 6,6′-di-*O*-trityl-*allo*-sucrose hexa-acetate (**10**), and a mono-*O*-trityl fraction, in yields of 10, 26, and 20%, respectively. The last fraction was shown by t.l.c. to contain at least two components. Hydrogenolysis of the ditrityl ether **10** gave the diol **12** with no detectable migration of acetyl groups, since re-tritylation of **12** gave **10** in high yield. Similarly, hydrogenolysis of the tritrityl ether **9** afforded the 6,1′,6′-triol penta-acetate which,

TABLE II

^{13}C-CHEMICAL SHIFTS IN P.P.M. DOWNFIELD FROM Me_4Si

Atom	**2**[a] *(D_2O)*	**3** *($CDCl_3$)*	**5**[a] *(D_2O)*	**8** *($CDCl_3$)*
C-2′	104.8	103.95	104.8	103.95
C-1	92.9	89.6	92.9	89.6
C-5′	82.4	78.75	82.3	78.75
C-3′	77.45	75.85	77.35	75.95
C-4′	74.7	75.05	74.7	75.05
C-3	72.0	67.15	—	—
C-2	67.6	66.70	67.55	66.65
C-5	68.7	65.75	68.7	65.75
C-4	66.6	64.75	66.5	64.75
C-6′	63.0	63.4	63.0	63.4
C-1′	62.4	63.9	62.4	63.9
C-6	61.2	62.1	61.2	62.1

[a]D.S.S. was used as the internal standard, and the above values were obtained by subtracting 1.7 from print-out values.

with sulphuryl chloride at −75°, gave 21% of the 6,1′,6′-trichloride **14**. The ^{1}H-n.m.r. spectrum of **14** confirmed the structure, and hence the absence of acetyl migration; H-4 resonated as a quartet at τ 4.98 ($J_{3,4}$ 3.5 and $J_{4,5}$ 10.0 Hz) which is characteristic of a D-allopyranoside. The reaction of *allo*-sucrose (**2**) with sulphuryl chloride in chloroform–pyridine at −50° for 4 h, followed by de-chlorosulphation and acetylation, gave, as with sucrose[14], a 6,6′-dichloride (**15**) in 9% yield after isolation by column chromatography.

EXPERIMENTAL

General. — 3-Ketosucrose (**1**) was prepared microbiologically by M.R.E. (Porton Down, Salisbury, Great Britain) and supplied in the form of a frozen, aqueous solution containing 4.9 g of **1** per litre (as determined by the method of Fukui and Hayano[15]) in the presence of nutrients and buffer, as described by Kurowski and Pirt[16]. Paper electrophoresis was performed in borate buffer (pH 10) at 350 V. Descending paper chromatography was performed on Whatman No. 1 paper with butanone–acetone–water (3 : 1 : 0.6), and alkaline silver nitrate[17] or urea phosphate[18] for detection. Auto-analysis of sugars was performed on a Technicon auto-analyser as previously described[3]. Column chromatography was performed on Kieselgel 7734 (Merck, 70–230 mesh). ^{13}C-N.m.r. spectra were recorded on a Bruker WP-60/DS spectrometer, as previously described[19].

β-D-*Fructofuranosyl* α-D-ribo-*hexopyranosid-3-ulose* (**1**). — The crude solution of **1** (100 ml, 0.49 g) from microbiological growth was added to a column[2] (8 × 4 cm) of charcoal (B.D.H. activated, acid-washed). Elution with water removed inorganic material and fructose, as evidenced by paper chromatography, and elution

with 10% aqueous ethanol then gave chromatographically pure **1** (0.35 g), $[\alpha]_D$ +22.5° (*c* 0.2, water); lit.[20] $[\alpha]_D$ +40.0° (trihydrate).

α-D-*Allopyranosyl* β-D-*fructofuranoside* (**2**). — (*a*) An aqueous solution (1 litre) of **1** (4.9 g) was treated with an excess of sodium borohydride at 0–5° for 24 h; paper chromatography then showed that reaction was complete. Excess of borohydride was decomposed with acetic acid, the solution was concentrated, and boric acid was removed by continuous distillation of methanol from the residue. The resulting gum was then treated with acetic anhydride–sodium acetate at 100° for 2 h and the crude acetate isolated in the usual manner. Fractionation on a column of silica gel (350 g), with ether–light petroleum (4:1), gave the octa-acetate **3** as a syrup (6 g, 80%), $[\alpha]_D$ +39° (*c* 1.45, chloroform) (Found: C, 49.3; H, 5.5. $C_{28}H_{38}O_{19}$ calc.: C, 49.6; H, 5.6%).

A solution of **3** (3 g) in dry methanol (150 ml) was treated with sodium (0.1 g). After 1 h, when deacetylation was complete, the solution was neutralised with Amberlite IR-120 (H^+) resin, decolourised with charcoal, and concentrated, to give **2** as a foam (1.2 g, 88%), M_{GLC} 0.4 (Found: C, 42.6; H, 6.5. $C_{12}H_{22}O_{11}$ calc.: C, 42.1; H, 6.4%).

Examination of an acid hydrolysate (0.1M sulphuric acid) of **2** by paper chromatography and by auto-analysis[3] showed the presence of allose and fructose.

Benzoyl chloride (0.4 ml) was added to a cooled solution (0°) of **2** (0.1 g) in dry pyridine (4 ml), which was then kept at room temperature overnight. The product was isolated in the usual manner by pouring into ice–water and extracting with chloroform, to give the octabenzoate **4** (0.25 g, 79%), m.p. 85–87° (from methanol), $[\alpha]_D$ +70.1° (*c* 0.33, chloroform) (Found: C, 70.2; H, 4.8. $C_{68}H_{54}O_{19}$ calc.: C, 69.8; H, 4.6%).

(*b*) To a solution of sucrose (7.5 g) in dimethyl sulphoxide (90 ml) was added acetic anhydride (60 ml). The solution was stirred at 60° for 0.5 h, cooled, diluted with chloroform (300 ml), and extracted with water (300 ml). The aqueous phase was extracted with chloroform (2 × 300 ml), cooled to 0°, and treated dropwise with 2M aqueous sodium borohydride (250 ml) during 2 h. The reaction mixture was stored overnight at 0°, excess of borohydride was then decomposed by addition of acetic acid, the solution was concentrated, and boric acid was removed by repeated distillation of methanol from the residue. A solution of the resulting syrup in a little water was added to a column (2.5 × 35 cm) of Dowex-50 X8 (Ca^{2+}) resin. Elution with water gave initially (t.l.c.) sucrose-containing fractions which were discarded. The *allo*-sucrose fractions were combined and concentrated to a syrup. Conventional benzoylation (benzoyl chloride–pyridine) and fractionation on silica gel (55 g) with ether–light petroleum (3:1) gave, initially, some fast-moving products which were discarded, followed by the octabenzoate **4** (1.28 g, 5%), m.p. and mixture m.p. 85–87°, $[\alpha]_D$ +70.6° (*c* 0.4, chloroform).

[*3*-^2H]allo-*Sucrose octa-acetate* (**8**) *and* [*3*-^2H]*sucrose octa-acetate* (**7**). — A solution of **1** (0.25 g) in water (10 ml) at 0° was treated with sodium borodeuteride (15 mg) during 30 min. The mixture was then stirred for 3 h at 0–5°, and excess of

borodeuteride was decomposed with acetic acid. T.l.c. (ethyl acetate–ethanol–water, 5:4:3) then showed one major and one minor component. The solution was concentrated and boric acid was removed by distillation of methanol from the residue, which was then eluted with water from a column (10 × 1 cm) of Dowex-50 X8 (Ca^{2+}) resin. Fractions (10 ml) were collected, and monitored by t.l.c. Initial fractions contained [3-^{2}H]sucrose (**6**) which, on conventional acetylation, gave the octa-acetate **7** (40 mg, 8%), $[\alpha]_D$ +59.5° (*c* 0.4, chloroform) (Found: C, 49.5; H, 5.5. $C_{28}H_{37}DO_{19}$ calc.: C, 49.4; H, 5.7%). Eluted second was [3-^{2}H]*allo*-sucrose (**5**) which, on acetylation, gave the octa-acetate **8** (360 mg, 72%), $[\alpha]_D$ +39.4° (*c* 0.6, chloroform) (Found: C, 48.6; H, 5.6. $C_{28}H_{37}DO_{19}$ calc.: C, 49.4; H, 5.7%).

*2,3,4-Tri-*O*-acetyl-6-*O*-trityl-α-*D*-allopyranosyl 3,4-di-*O*-acetyl-1,6-di-*O*-trityl-β-*D*-fructofuranoside* (**9**) *and 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-*D*-allopyranosyl 1,3,4-tri-*O*-acetyl-6-*O*-trityl-β-*D*-fructofuranoside* (**10**). — A solution of trityl chloride (2.51 g) in dry pyridine (20 ml) was added dropwise during 1 h to a solution of *allo*-sucrose (1.03 g) in pyridine (40 ml). The mixture was stirred for 2 days at room temperature, acetic anhydride (6 ml) was added, and the mixture was kept overnight and then poured into ice–water. The resulting precipitate was filtered off, washed well with water, and dried. T.l.c. (ether–light petroleum, 3:1) showed it to contain at least three major products. Elution from silica gel (80 g) with ether–light petroleum (1:1) gave, first, the penta-acetate **9** (0.38 g, 10%), m.p. 218°, $[\alpha]_D$ +54.0° (*c* 0.3, chloroform) (Found: C, 74.3; H, 6.1. $C_{79}H_{74}O_{16}$ calc.: C, 74.2; H, 5.8%). Eluted second was the hexa-acetate **10** (0.84 g, 26%), m.p. 175–177°, $[\alpha]_D$ +45.9° (*c* 0.2, chloroform) (Found: C, 69.45; H, 5.55. $C_{62}H_{62}O_{17}$ calc.: C, 69.0; H, 5.75%). Eluted third was a monotrityl-*allo*-sucrose hepta-acetate fraction (0.17 g, 20%), m.p. 145–160°, $[\alpha]_D$ +62.2° (*c* 1.23, chloroform) (Found: C, 62.1; H, 5.9. $C_{45}H_{50}O_{18}$ calc.: C, 61.5; H, 5.7%). *O*-Deacetylation of the monotrityl fraction with 0.1M methanolic sodium methoxide gave (t.l.c.; ether–methanol, 15:1) at least two products.

*6-*O*-Trityl-α-*D*-allopyranosyl 1,6-di-*O*-trityl-β-*D*-fructofuranoside* (**11**). — A solution of the penta-acetate **9** (100 mg) in dry methanol (10 ml) was treated with 0.1M methanolic sodium methoxide (1 ml). After being kept at room temperature for 3 h, the solution was neutralised with Amberlite IR-120 (H^+) resin and concentrated, to give **11** as an amorphous solid (80 mg, 95%), $[\alpha]_D$ +46.8° (*c* 0.4, methanol) (Found: C, 76.9; H, 5.9. $C_{69}H_{64}O_{11}$ calc. C, 77.5; H, 5.9%).

*2,3,4-Tri-*O*-acetyl-α-*D*-allopyranosyl 1,3,4-tri-*O*-acetyl-β-*D*-fructofuranoside* (**12**). — A solution of the hexa-acetate **10** (300 mg) in ethanol–chloroform (1:1, 10 ml) was hydrogenated over platinum–charcoal until t.l.c. showed that **10** was no longer present. The mixture was filtered and concentrated to a syrup that was dissolved in toluene (15 ml) and extracted with water (4 × 10 ml). The aqueous solution was extracted with chloroform (40 ml), and the chloroform solution was dried (Na_2SO_4), filtered, and concentrated, to give the hexa-acetate **12** as a syrup (120 mg, 76%), $[\alpha]_D$ +36.5° (*c* 0.3, chloroform) (Found: C, 49.5; H, 5.5. $C_{24}H_{34}O_{17}$ calc.: C, 48.5; H, 5.7%).

A solution of **12** (0.09 g) in dry pyridine (3 ml) was treated with trityl chloride

(0.11 g) for 3 days at room temperature. T.l.c. (ethanol) indicated the presence of a fast-moving component. The reaction mixture was poured into ice–water, extracted with chloroform, and worked-up in the usual manner, to give a syrup. Chromatography on a column of silica gel (10 g) with ether–light petroleum (3 : 1) then gave **10** (0.13 g, 79%), m.p. and mixture m.p. 175–177°. The i.r. spectrum was identical with that of **10** prepared above.

The hexa-acetate **12** (100 mg) in dry pyridine (3 ml) was treated with mesyl chloride (0.05 ml). After 24 h, the reaction mixture was poured into ice–water, and the precipitate was filtered off, washed well with water, and dried, to give the 6,6′-dimesylate **13** (190 mg, 75%), $[\alpha]_D$ +43.2° (*c* 0.28, chloroform) (Found: C, 41.9; H, 5.0; S, 9.2. $C_{26}H_{38}O_{21}S_2$ calc.: C, 41.6; H, 5.1; S, 8.6%).

*2,3,4-Tri-*O*-acetyl-6-chloro-6-deoxy-α-*D*-allopyranosyl 3,4-di-*O*-acetyl-1,6-dichloro-1,6-dideoxy-β-*D*-fructofuranoside* (**14**). — The penta-acetate **9** (0.25 g) in ethanol–chloroform (2:1, 15 ml) was hydrogenated over platinum–charcoal until t.l.c. showed the absence of **9**. The mixture was filtered, the filtrate concentrated, and a solution of the syrupy residue in toluene (25 ml) extracted with water (2 × 10 ml). The aqueous solution was extracted with chloroform (4 × 10 ml), and the chloroform extract was dried ($MgSO_4$) and concentrated to a syrup (72 mg) which was dissolved in a 2:1 mixture (5 ml) of pyridine and ethanol-free chloroform. The solution was cooled to −75° (acetone–solid CO_2), redistilled sulphuryl chloride (0.1 ml) was added, and the mixture was stirred at −75° for 4 h, and then allowed to attain room temperature. T.l.c. (ether) showed the presence of a fast-moving product. The reaction mixture was poured into ice–2M hydrochloric acid, and the chloroform layer was separated, washed successively with water, aqueous sodium hydrogencarbonate, and water, dried ($MgSO_4$), and concentrated to a syrup, which was fractionated on silica gel (10 g) with ether–light petroleum (3 : 1), to give the 6,1′,6′-trichloride **14** (25 mg, 21%) (Found: C, 43.3; H, 4.7; Cl, 17.6. $C_{22}H_{29}Cl_3O_{13}$ calc.: C, 43.5; H, 4.8; Cl, 17.5%).

*2,3,4-Tri-*O*-acetyl-6-chloro-6-deoxy-α-*D*-allopyranosyl 1,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-β-*D*-fructofuranoside* (**15**). — Sulphuryl chloride (8 g) was added dropwise, during 0.5 h, to a stirred suspension of *allo*-sucrose (1.04 g) in chloroform (8 ml) and dry pyridine (8 ml) at −50°. After a further 4 h at this temperature, the reaction mixture was filtered into a stirred suspension of sodium carbonate (10 g) in methanol (100 ml) containing a catalytic amount of sodium iodide. The mixture was stirred for 2 h and filtered, the filtrate was concentrated to dryness, and the residue was dissolved in pyridine (20 ml) and treated with acetic anhydride (6 ml). The mixture was kept at room temperature for 24 h, and then poured into ice–water, extracted with chloroform (20 ml), and worked-up in the usual manner to give a syrup. T.l.c. (ether) indicated one major and several minor products. Fractionation by elution from silica gel with ether–light petroleum (1 : 1) gave the hexa-acetate **15** (0.17 g, 8.9%), $[\alpha]_D$ +44.5° (*c* 0.4, chloroform) (Found: C, 45.55; H, 5.0; Cl, 11.3. $C_{24}H_{32}Cl_2O_{15}$ calc.: C, 45.6; H, 5.1; Cl, 11.2%).

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REFERENCES

1 M. J. BERNAERTS, J. FURNELLE, AND J. DELEY, *Biochim. Biophys. Acta*, 69 (1963) 322–330.
2 P. ANDREWS, L. HOUGH, AND D. B. POWELL, *Chem. Ind. (London)*, (1956) 10.
3 L. HOUGH, J. V. S. JONES, AND P. WUSTEMAN, *Carbohydr. Res.*, 21 (1972) 9–17.
4 B. LINDBERG AND K. N. SLESSOR, *Acta Chem. Scand.*, 21 (1967) 910–914.
5 M. E. EVANS AND S. J. ANGYAL, *Carbohydr. Res.*, 25 (1972) 43–48.
6 P. A. J. GORIN, *Can. J. Chem.*, 52 (1974) 458–461.
7 H. SPIESECKE AND W. G. SCHNEIDER, *J. Chem. Phys.*, 35 (1961) 731–738.
8 F. J. WEIGERT AND J. D. ROBERTS, *J. Am. Chem. Soc.*, 89 (1967) 2967–2969.
9 G. L. LEBEL, J. D. LAPOSA, B. G. SAYER, AND R. A. BELL, *Anal. Chem.*, 43 (1971) 1500–1501.
10 Y. K. GRISHIN, N. M. SERGEYEV, AND Y. A. USTYNYUK, *Mol. Phys.*, 22 (1971) 711–714.
11 D. DODDRELL AND I. BURFITT, *Aust. J. Chem.*, 25 (1972) 2239–2241.
12 R. A. BELL, C. L. CHAN, AND B. G. SAYER, *Chem. Commun.*, (1972) 67.
13 (*a*) A. ALLERHAND AND D. DODDRELL, *J. Am. Chem. Soc.*, 93 (1971) 2777–2779; (*b*) F. R. SEYMOUR, R. D. KNAPP, J. E. ZWEIG, AND S. H. BISHOP, *Carbohydr. Res.*, 72 (1979) 57–69; (*c*) P. E. PFEFFER, K. M. VALENTINE, AND F. W. PARRISH, *J. Am. Chem. Soc.* 101 (1979) 1265–1274.
14 J. M. BALLARD, L. HOUGH, A. C. RICHARDSON, AND P. FAIRCLOUGH, *J. Chem. Soc., Perkin Trans. 1*, (1973) 1524–1528.
15 S. FUKUI AND K. HAYANO, *Agric. Biol. Chem.*, 32 (1969) 1013–1017.
16 W. M. KUROWSKI AND S. J. PIRT, *J. Gen. Microbiol.*, 68 (1971) 65–69.
17 W. E. TREVEYLAN, D. P. PROCTER, AND J. S. HARRISON, *Nature (London)*, 166 (1950) 444–445.
18 C. S. WISE, R. J. DIMLER, H. A. DAVIS, AND C. E. RIST, *Anal. Chem.*, 27 (1955) 33–36.
19 L. HOUGH, S. P. PHADNIS, AND E. TARELLI, *Carbohydr. Res.*, 47 (1976) 151–154.
20 S. FUKUI, R. M. HOCHSTER, R. DURBIN, E. E. GREBNER, AND D. S. FEINGOLD, *Bull. Res. Counc. Isr.*, 1144 (1963) 262–268.