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THE REACTION OF RAFFINOSE WITH SULPHURYL CHLORIDE*

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ABSTRACT

The reaction of raffinose with sulphuryl chloride in a mixture of pyridine and chloroform at temperatures between ambient and −20° afforded, after dechlorosulphation, 6′-chloro-6′-deoxyraffinose†, 6′,6″-dichloro-6′,6″-dideoxyraffinose, 6-*O*-(4,6-dichloro-4,6-dideoxy-α-D-glucopyranosyl)-α-D-glucopyranosyl 6-chloro-6-deoxy-β-D-fructofuranoside, methyl 6-chloro-6-deoxy-α-D-fructofuranoside, and methyl 6-chloro-6-deoxy-β-D-fructofuranoside The proportions of these products depended on the reaction conditions, higher temperatures and longer reaction times favoured the formation of the monosaccharide derivatives, which, under certain conditions, could be isolated in a combined yield of 51 % Catalytic hydrogenolysis of 6′-chloro-6′-deoxyraffinose and the foregoing trichloro derivative afforded, respectively, 6′-deoxyraffinose and 6′,4″,6″-trideoxyraffinose in good yields

INTRODUCTION

The reaction between sulphuryl chloride and carbohydrates was first described[2] by Helferich in 1921, who noted that certain hydroxyl groups were replaced by chlorine and that others were engaged in the formation of cyclic sulphate esters The mechanism and the stereochemistry of the process were not understood until J K N Jones and his colleagues undertook a thorough study of the reaction[3] They showed that the reaction proceeded *via* chlorosulphate esters ($ROSO_2Cl$), some of which underwent bimolecular nucleophilic substitution by chloride to give chlorodeoxy derivatives The chlorosulphate groups that undergo replacement by chloride are those which would be expected to undergo S_N2 displacement by nucleophiles according to the rules proposed by Richardson[4] We have applied this reaction to disaccharide derivatives, including trehalose[5], sucrose[6], methyl β-maltoside[7], methyl β-lactoside[8], and benzyl β-cellobioside[9], and obtained a variety of chloro derivatives that have been employed as synthetic intermediates for the preparation of deoxy, amino, and

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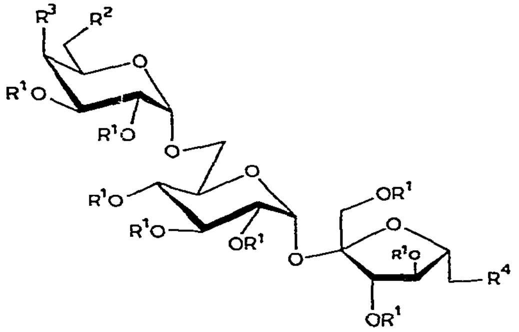
*Raffinose Chemistry Part II For Part I, see Ref 1
†The unprimed, single-primed, and double-primed numbers refer to the carbon atoms in the D-glucosyl, D-fructosyl, and D-galactosyl rings, respectively

azido derivatives The introduction of chlorine atoms at certain positions of the sucrose molecule has a profound effect upon the sweetness of the disaccharide, and, for example, the 4,6,1′,6′-tetrachloro derivative is 200 times sweeter than sucrose[10]. Consequently, it was of interest to study the reaction of oligosaccharides related to sucrose with sulphuryl chloride, in order to prepare a wider range of chlorinated oligosaccharides related to the intensely sweet chloro-sucroses We now describe the reaction of raffinose (6-*O*-α-D-galactopyranosylsucrose) with sulphuryl chloride.

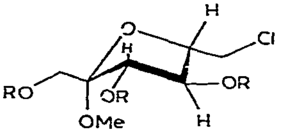
RESULTS AND DISCUSSION

The reaction of raffinose (**1**) with sulphuryl chloride at —20° for 5 h gave, after dechlorosulphation (with methanolic sodium iodide in the presence of sodium carbonate) and acetylation, a mixture containing one major and several minor components Chromatographic fractionation of this mixture afforded five pure components (*A*–*E*)

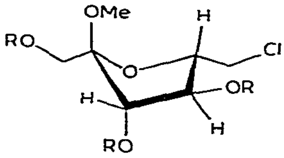
The fastest-moving component (*A*) was isolated in 6% yield as a syrup Elemental analysis and spectroscopic studies indicated *A* to be methyl 1,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-*β*-D-fructofuranoside (**12**) The mass spectrum contained intense signals at *m*/*e* 265 and 307, due to loss of CH_2OAc and OMe, respectively,



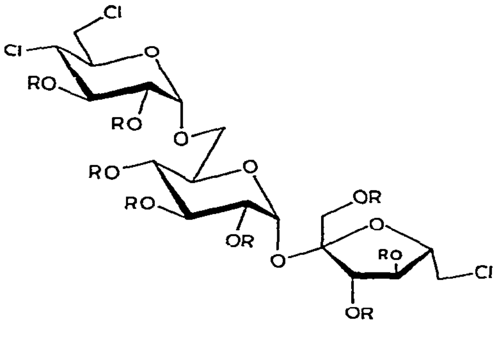
1 $R^1 = H, R^2 = R^3 = R^4 = OH$
2 $R^1 = Ac, R^2 = R^4 = Cl, R^3 = OAc$
3 $R^1 = H, R^2 = R^4 = Cl, R^3 = OH$
4 $R^1 = Ac, R^2 = R^3 = OAc$ $R^4 = Cl$
5 $R^1 = H, R^2 = R^3 = OH, R^4 = Cl$
6 $R^1 = R^4 = H, R^2 = R^3 = OH$
7 $R^1 = Ac, R^2 = P^3 = OAc$ $R^4 = H$
8 $R^1 = Ac, R^2 = R^3 = R^4 = H$
9 $R^1 = R^2 = R^3 = R^4 = H$
10 $R^1 = Ac$, $R^2 = Cl, R^3 = R^4 = H$
11 $R^1 = H$, $R^2 = Cl$ $R^3 = R^4 = H$



12 R = Ac
13 R = H



14 R = Ac
15 R = H



16 R = Ac
17 R = H

TABLE I

^{13}C-CHEMICAL SHIFTS[a] OF METHYL 6-CHLORO-6-DEOXYFRUCTOFURANOSIDES

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Methyl*
Methyl 6-chloro-6-deoxy-β-D-fructofuranoside (**13**)	62 2	106 6	79 4	83 4	78 7	47 9	51 7
Methyl 6-chloro-6-deoxy-α-D-fructofuranoside (**15**)	60 4	111 1	84 9	82 7	81 1	46 7	51 0

[a] P p m downfield from DSS

from the molecular ion, thereby indicating that *A* was a fructoside and that the chlorine atom was not at C-1. The presence of the chlorine atom at C-6 was indicated by the ^{1}H-n m r spectrum in which the H-6a and H-6b resonances were centred around τ 6 5, indicating a CH_2Cl group All other resonances were in agreement with the proposed structure, and the values for $J_{3\,4}$ (6 Hz) and $J_{4\,5}$ (7 Hz) were similar to those observed for sucrose derivatives and therefore suggested the β-anomeric configuration

The second fraction *B*, obtained in 5% yield, was the α anomer of the fructofuranoside **12** The mass spectra of *B* and **12** were almost superposable, but the ^{1}H-n m r spectrum of *B* showed coupling constants $J_{3\,4}$ 2 Hz and $J_{4\,5}$ 5 Hz which were distinctly different from those found for sucrose derivatives Therefore, the data are in agreement with the α anomer **14** Careful deacetylation of each anomer gave the methyl 6-chloro-6-deoxy-D-fructofuranosides **13** and **15**, for which the ^{13}C-n m r parameters are given in Table I Notably, the C-2 resonances differ by 4 5 p p m , which is consistent with a change of stereochemistry at this position

The third component *C*, obtained in 10% yield, was a crystalline trichloro derivative of raffinose Examination of an acid hydrolysate of the deacetylated material by paper chromatography revealed the presence of glucose, but no galactose or fructose, showing that the three chloro groups were located on fructosyl and galactosyl residues The mass spectrum of *C* contained peaks for three oxycarbonium ions at *m/e* 283 (2 Cl), 307 (1 Cl), and 571 (2 Cl) due to two hexosyl cations and a disaccharidyl cation, respectively In particular, the ions at *m/e* 571 and 283 clearly indicated that two chlorine atoms were present on the galactosyl ring, and the ion at *m/e* 307 must be due to the fructosyl residue having a single chlorine substituent Finally, the positions of the chlorine atoms were determined by an examination of the ^{13}C-n m r spectrum (Table II) of the deacetylated compound (**17**), the C-4″, C-6″, and C-6′ resonances were shifted to high field by ~10, 16, and 17 p p m , respectively, in comparison with those of raffinose (**1**), in agreement with the assigned structure of **16**

Component *D* crystallised in 7% overall yield, and elemental analysis indicated that it was a dichloro derivative of raffinose Its mass spectrum showed intense

TABLE II

^{13}C-CHEMICAL-SHIFT DATA[a]

Carbon atom	**1**[b]	**3**	**5**	**6**	**9**	**11**	**17**
C-2	106 37	106 70	106 65	106 17	106 63	106 63	106 62
C-1″	101 09	101 15	101 19	101 09	101 90	101 41	101 09
C-1	94 66	95 06	94 95	94 60	94 98	94 86	94 92
C-4′	83 89	83 35	83 32	81 35	81 88	83 22	83 21
C-3′	79 01	79 21	79 22	80 01	80 73	79 07	79 36
C-5′	76 60	78 54	78 51	78 94	79 58	78 40	78 52
C-2	75 26	75 40	75 26	—	76 42	75 59	75 46
C-3	74 99	74 06	74 09	73 86	76 06	75 19	75 46
C-5	73 59	73 66	73 57	73 66	74 24	73 98	74 40
C-5″	72 05	72 25	72 20	72 12	72 78	73 58	74 40
C-2′ }	71 85	72 05	71 81	71 85	70 36	72 11	73 61
C-4 }							72 35
C-4″	71 05	70 85	71 03	71 12	42 94	39 86	61 59
C-3″	69 09	69 04	69 08	—	69 02	70 77	69 34
C 6	68 51	—	—	68 56	68 05	68 77	—
C-6′	65 03	48 03	48 03	20 89	22 81	22 20	48 03
C-1′	64 02	63 89	63 69	64 16	64 78	63 82	63 96
C-6″	63 69	45 76	63 69	63 69	21 23	47 89	47 30

[a] P p m downfield from DSS [b] For ^{13}C-assignments, see Ref 12

peaks for only two oxycarbonium ions at *m/e* 307 (1 Cl) and 595 (1 Cl), indicating that the galactopyranosyl and fructofuranosyl residues must contain one chlorine atom each This observation was substantiated by acid hydrolysis of the deacetylated compound **3** which gave (paper chromatography) glucose as the only unsubstituted monosaccharide Comparison of the ^{13}C-n m r spectrum (Table II) of **3** with that of raffinose (**1**) showed shifts of the C-6′ and C-6″ resonances to high field by $\sim$17 and 18 p p m , respectively On the basis of these results, *D* was identified as the 6′6″-dichloride **2**

The major component (*E*) was obtained crystalline in 43% yield and shown to be 6′-chloro-6′-deoxyraffinose deca-acetate (**4**) The mass spectrum of **4** contained three intense signals for oxycarbonium ions at *m/e* 307 (1 Cl), 331, and 619 due to two hexosyl cations and a disaccharidyl cation, respectively, since the latter indicated the absence of chlorine, the single chlorine substituent was assigned to the fructofuranosyl ring Careful de-esterification of **4** gave a hygroscopic compound **5** which, upon acid hydrolysis, afforded galactose and glucose, but no fructose The structure of **5** was confirmed by ^{13}C-n m r spectroscopy (Table II), which revealed an upfield shift of the C-6′ resonance by 17 p p m , compared to that of raffinose

In an attempt to increase the yields of di-, tri-, and higher chlorinated products, the reaction period of raffinose with sulphuryl chloride was extended. After 7 h, the di- and tri-chlorides **2** and **16** were isolated in yields of 20 and 13%, respectively

However, when the reaction time was extended to 18 h, the methyl fructofuranosides **12** and **14** were isolated in yields of 27% and 24%, respectively

It is noteworthy that formation of the methyl fructofuranosides **13** and **15** appears to be a major pathway in the reaction, whereas these products have not been detected when sucrose was similarly treated with sulphuryl chloride Indeed, much more extensive chlorination of sucrose was observed and two penta- and one hexa-chlorinated sucroses were isolated[6] The reason for these differences between sucrose and raffinose remains obscure It is possible that **13** and **15** arise by cleavage of the glucose–fructose glycosidic bond during the chlorination to give, as one of the products, the fructofuranosyl chloride Subsequent dechlorosulphation in methanol would then give rise to the methyl fructofuranosides **13** and **15** Jennings[15] observed that dechlorosulphation of α-D-xylopyranosyl chloride trischlorosulphate in methanol similarly afforded the methyl xylopyranosides

The $J_{3,4}$ values for **12** and **14** (6 and 2 Hz, respectively) correspond to dihedral angles of ~140–150° for the β anomer and 100–110° for the α anomer This large difference is explicable in terms of the existence of the α anomer in the E_1 conformation with the 2-methoxyl group *pseudo*-axial (anomeric effect) and the chloromethyl group *pseudo*-equatorial as in **14** On the other hand, the β anomer adopts the E^1 conformation, which maintains the 2-methoxyl group axial as in **12**

Reductive dehalogenation of the 6′-chloride **5** with Raney nickel in the presence of a stoichiometric amount of potassium hydroxide gave one major product, as indicated by t l c It was isolated in 27% yield and characterised as 6′-deoxyraffinose deca-acetate (**7**) The mass spectrum of **7** contained strong signals for two hexosyl oxycarbonium ions and a disaccharidyl oxycarbonium ion at *m/e* 331, 273, and 619, respectively, due to cleavage of the galactopyranosyl, deoxyfructofuranosyl, and melibiosyl bonds, respectively The assigned structure of **7** was further confirmed by the ^{13}C-n m r spectrum (Table II) of the deacetylated compound (**6**), which showed a large upfield shift of the C-6′ resonance by 44 p p m with the positions of the other primary carbon resonances unaltered

Surprisingly, 6′-chlororaffinose (**5**) was also reductively dehalogenated by Raney nickel in the presence of triethylamine, and the product was isolated in 54% yield It has previously been noted that only secondary chlorine substituents are reduced in the presence of triethylamine, and that dehalogenation of primary chloro groups requires potassium hydroxide as base

Similarly, reduction of the 6′,4″,6″-trichloride **17** in the presence of potassium hydroxide afforded the trideoxyraffinose **9**, which was isolated as its octa-acetate **8** in 51% yield The structure of **9** was elucidated by the application of ^{13}C-n m r and mass spectrometry Thus, the ^{13}C-n m r spectrum (Table II) of the deacetylated compound showed high-field shifts for the C-4″, C-6″, and C-6′ resonances by 28, 42, and 42 p p m , respectively The mass spectrum of the octa-acetate **8** contained signals for three oxycarbonium ions at *m/e* 273, 215, and 503 due to deoxyfructofuranosyl, dideoxygalactopyranosyl, and dideoxymelibiosyl cations, respectively When the hydrogenation of **17** was repeated in the presence of triethylamine, it gave the 6″-chloro-6′,4″,6″-trideoxyraffinose **11**, best isolated as its octa-acetate **10** The ^{13}C-n m r spectrum (Table II) of **11**, in comparison with that of raffinose, showed upfield shifts of the C-4″, C-6″, and C-6′ resonances by 33, 16, and 43 p p m , respectively, which is in accord with the assigned structure This conclusion was confirmed by the mass spectrum of **10**, which showed very intense peaks for oxycarbonium ions at *m/e* 249 (1 Cl), 273, and 537 (1 Cl) due to chlorodideoxygalactopyranosyl, deoxyfructofuranosyl, and chlorodideoxymelibiosyl cations, respectively.

EXPERIMENTAL

General methods — Evaporations were carried out under reduced pressure below 45° Optical rotations were determined on chloroform solutions (unless otherwise stated) with a Perkin–Elmer 141 polarimeter and a 1-dm tube Melting points were determined on a Kofler hot-stage and are uncorrected Silica Gel 7731 (Merck) was used for t l c , detection being effected by charring with sulphuric acid Dry-column chromatography was performed on Silica Gel 7734 (Merck) Anhydrous pyridine was prepared by distillation from calcium hydride Chloroform and methanol were dried over magnesium sulphate Light petroleum (b p 60–80°) was used throughout Chlorination reactions were monitored by withdrawing aliquots of the reaction mixture and adding them to a suspension of sodium carbonate in methanol containing a catalytic amount of sodium iodide, in order to effect dechlorosulphation All reductions were carried out at room temperature and 60 p s i in the presence of Raney-nickel catalyst All deacetylated chlorodeoxy and deoxy compounds were hydrolysed in 6M hydrogen chloride at room temperature and then neutralised with Amberlite IR-45 (HO$^-$) resin Paper chromatograms were developed in 1-butanol–toluene–pyridine–water (5 1 3 3) and processed as described by Hough *et al*[14] ^{1}H-N m r spectra were recorded with a Varian HA-100 instrument at 100 MHz Selected regions of the spectra (τ 4–7) were then recorded at 220 MHz with a Varian HR-220 spectrometer, Me_4Si was used as the internal standard Mass spectra were determined with an A E I MS-30 spectrometer at 70 eV ^{13}C-N m r spectra were recorded with a Bruker-WP-60 instrument Solutions of concentration 50–100 mg/ml made up in D_2O were used throughout with DSS as the internal standard The sample temperature in each case was 34 ±2° Raffinose pentahydrate was dried at 70°/8 mmHg for 24 h and then dissolved in pyridine, and the solution was evaporated to azeotropically distil off the remaining water. The latter process was repeated five times

Reaction of raffinose with sulphuryl chloride — (*a*) To a stirred suspension of raffinose (**1**, 10 g, 19 8 mmol) in a mixture of chloroform (100 ml) and pyridine (40 ml) at −78° was added sulphuryl chloride (30 ml, 371 mmol) dropwise during 1 h After 2 h, the mixture was allowed to warm up to between −10 and −20° and maintained thereat for 5 h The mixture was then poured into methanol (500 ml) containing sodium carbonate (20 g) and sodium iodide (1 g), stirred for 3 h, filtered, and concentrated to dryness The resulting yellow solid (17 g) was dissolved in pyridine (170 ml), and acetic anhydride (25 ml) was added dropwise After 12 h, when t l c (ether–light petroleum, 8 1) showed a mixture of at least eight components, the reaction mixture was poured into ice–water and extracted with dichloromethane, and the extract was dried ($MgSO_4$) and evaporated to dryness, pyridine was removed azeotropically with toluene The resulting syrup was fractionated on a column of silica gel with ether–light petroleum (4 1)

Component *A*, eluted first, was syrupy methyl 1,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-β-D-fructofuranoside (**12**, 0.42 g, 6%), $[\alpha]_D$ −33° (*c* 1 12) (Found C, 45 3, H, 6 2, Cl, 10 5 $C_{13}H_{19}ClO_8$ calc C, 46 1, H, 5 6, Cl, 10 45%) ^{1}H-N m r data (C_6D_6, 220 MHz) τ 4 26 (d, 1 H, $J_{3\ 4}$ 6 0 Hz, H-3), 4 42 (dd, 1 H, $J_{4\ 5}$ 7 Hz, H-4), 5 7 (m, 2 H, H-1a,1b), 5 84 (dt, 1 H, $J_{5\ 6a}$ 5, $J_{5\ 6b}$ 7 5 Hz, H-5), 6 40 (dd, 2 H, $J_{6a,6b}$ 11 5 Hz, H-6), 6 58 (dd, 2 H, H-6b), 6 92 (s, OMe), 8 24, 8 28, and 8 31 (3s, 9 H, 3 OAc) *O*-Deacetylation of **12** gave unstable methyl 6-chloro-6-deoxy-β-D-fructofuranoside (**13**), m p 96–98° (from methanol), $[\alpha]_D$ −29° (*c* 1, methanol) (Found C, 39 25, H, 6 05, Cl, 16 75 $C_7H_{13}ClO_5$ calc C, 39 55, H, 6 1, Cl, 16 7%)

Component *B*, eluted second, was syrupy methyl 1,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-α-D-fructofuranoside (**14**, 0 35 g, 5%), $[\alpha]_D$ +70° (*c* 1 34) (Found C, 46 5, H, 5 8, Cl, 10 5 $C_{13}H_{19}ClO_8$ calc C, 46 1, H, 5 6, Cl, 10 45%) ^{1}H-N m r data (C_6D_6, 100 MHz) τ 4 38 (d, 1 H, $J_{3\ 4}$ 2 Hz, H-3), 4 88 (dd, 1 H, $J_{4\ 5}$ 5 Hz, H-4), 5 5 (m, 2 H, H-1a,1b), 5 90 (m, 1 H, H-5), 6 45 (m, 2 H, H-6a,6b), 6 88 (s, OMe), 8 30, 8 32, and 8 28 (3s, 9 H, 3 OAc) Deacetylation of **14** gave unstable methyl 6-chloro-6-deoxy-α-D-fructofuranoside (**15**), m p 71–73°, (from methanol), $[\alpha]_D$ +40° (*c* 0 5, methanol) (Found C, 39 05, H, 6 3, Cl, 17 8 $C_7H_{13}ClO_5$ calc C, 39 55 H, 6 1, Cl, 16 7%)

Component *C*, eluted third, was crystallised from di-isopropyl ether–light petroleum to give the 6′,4″,6″-trichloro derivative **16** (1 78 g, 10%), m p 134–135°, $[\alpha]_D$ +81° (*c* 1) (Found C, 45 3, H, 5 3, Cl, 11 9 $C_{34}H_{45}Cl_3O_{21}$ calc C, 45 6, H, 5 0, Cl, 11 9%) Deacetylation of **16** gave the trichloride **17** as a hygroscopic foam, $[\alpha]_D$ +100° (*c* 1, methanol) (Found C 37 5. H, 5 2, Cl, 18 4 $C_{18}H_{29}Cl_3O_{13}$ calc C, 38 6, H, 5 2, Cl, 19 0%)

Component *D*, eluted fourth, was recrystallised from di-isopropyl ether–light petroleum to give the 6′,6″-dichloride **2** (1 82 g, 7%), m p 66–68°, $[\alpha]_D$ +110° (*c* 0 2) (Found C, 46 95, H, 5 6, Cl, 6 4 $C_{36}H_{48}Cl_2O_{23}$ calc C, 47 0, H, 5 2, Cl, 7 75%) Deacetylation of **2** afforded the dichloride **3** in high yield as an amorphous, hygroscopic powder, m p 109–112°, $[\alpha]_D$ +117° (*c* 0 5, methanol) (Found C, 38 1, H, 5 6, Cl, 12 5 $C_{18}H_{30}Cl_2O_{14}$ calc C, 39 9, H, 5 55, Cl, 13 1%)

Component *E*, eluted fifth, was the major component and was crystallised from di-isopropyl ether to give 6′-chloro-6′-deoxyraffinose deca-acetate (**4**, 8 g, 43%), m p 66–67°, $[\alpha]_D$ +99.5° (*c* 1) (Found C, 48 7, H, 5 5, Cl, 4 3 $C_{38}H_{51}ClO_{25}$ calc C, 48 4, H, 5 4, Cl, 3 75%) Deacetylation of the deca-acetate **4** gave 6′-chloro-6′-deoxyraffinose (**5**) as a very hygroscopic, hard syrup, $[\alpha]$ +118 8° (*c* 0 25, methanol), which did not give a satisfactory analysis

(*b*) Repetition of the reaction as in (*a*), except that the mixture was kept at

$-20°$ for 7 h rather than 5 h, gave a mixture of components *A*, *B*, *C*, and *D* isolated in yields of 20, 13, 21, and 17%, respectively.

(*c*) A stirred solution of raffinose (**1**; 10 g, 20 mmol) in a mixture of chloroform (100 ml) and pyridine (40 ml) was cooled to $-78°$ and treated with sulphuryl chloride (30 ml, 360 mmol) dropwise during 1 h. The mixture was allowed to warm up to room temperature, and was stirred constantly for 5 h. T.l.c. (chloroform–methanol, 3:1) then showed two major fast-moving, and some minor slow-moving, components. The mixture was then worked up, acetylated, and fractionated, as before, when *A* (**12**) and *B* (**14**) were isolated in yields of 27 and 24%, respectively.

6′-Deoxyraffinose (**6**). — (*a*) A solution of 6′-chloro-6′-deoxyraffinose (**5**, 0.33 g, 0.63 mmol) and potassium hydroxide (0.04 g, 0.7 mmol) in methanol (50 ml) was hydrogenated in the presence of Raney-nickel catalyst (5 g, wet) for 6 days; t.l.c. (chloroform–methanol, 1:1) then indicated the presence of a major, slow-moving product along with some minor components. The reaction mixture was filtered, neutralised [Amberlite IR-120(H$^+$)resin], and evaporated to dryness. The syrupy residue (0.4 g) was fractionated on silica gel (eluant chloroform–methanol, 3:1), to give **6** as an amorphous, hygroscopic powder (85 mg, 27%), m.p. 122–125°, $[\alpha]_D$ +48° (*c* 0.5, methanol).

Acetylation of **6** gave the deca-acetate **7** as an amorphous solid (74%), m.p. 65–68°, $[\alpha]_D$ +93° (*c* 0.5) (Found: C, 50.4; H, 5.6. $C_{38}H_{52}O_{25}$ calc.: C, 50.2; H, 5.7%).

(*b*) To a solution of the monochloride **5** (0.44 g, 0.84 mmol) in methanol (50 ml) was added triethylamine (3 ml, 21.6 mmol), and the mixture was hydrogenated and processed as in (*a*), to give **6** (0.22 g, 54.0%), m.p. and mixture m.p. 122–125°. The i.r. spectra of the two products were identical.

6′,4″,6″-Trideoxyraffinose octa-acetate (**8**). — The 6′,4″,6″-trichloride **17** (0.44 g, 0.8 mmol) and potassium hydroxide (0.16 g, 2.9 mmol) were dissolved in methanol (50 ml) and hydrogenated in the presence of Raney-nickel catalyst (6 g, wet) for 72 h; t.l.c. (ethyl acetate–ethanol–water, 10:3:2) then showed the presence of a single, major, slow-moving product. The reaction mixture was filtered through Hyflo supercel, neutralized [Amberlite IR-120(H$^+$)resin], and evaporated to dryness. Acetylation of the residue, in the usual way, gave the octa-acetate **8** as a white, amorphous powder (0.32 g, 51%), m.p. 56–59°, $[\alpha]_D$ +106° (*c* 0.5) (Found: C, 51.5; H, 6.1. $C_{34}H_{48}O_{21}$ calc.: C, 51.5; H, 6.1%). Deacetylation of the octa-acetate **8** afforded 6′,4″,6″-trideoxyraffinose (**9**) as a white, amorphous powder (81%), m.p. 108–111°, $[\alpha]_D$ +95° (*c* 0.24, methanol) (Found: C, 46.9; H, 6.9. $C_{18}H_{32}O_{13}$ calc.: C, 47.3; H, 7.0%).

6″-Chloro-6′,4″,6″-trideoxyraffinose octa-acetate (**10**). — A solution of the 6′,4″,6″-trichloride **17** (0.31 g, 0.55 mmol) and triethylamine (1 ml, 7.2 mmol) in methanol (100 ml) was hydrogenated in the presence of Raney-nickel catalyst (5 g, wet) for 21 h. T.l.c. (chloroform–methanol, 2:1) then indicated the presence of a slow-moving product. The reaction mixture was filtered, and concentrated to dryness, and the residue was acetylated, as described for **8**, to give the crystalline octa-acetate

10 (0 141 g, 31%), m p 56–59° (from ether–light petroleum), $[\alpha]_D$ +117° (*c* 0 5) (Found. C, 49 5; H, 6 0, Cl, 5 0 $C_{34}H_{47}ClO_{21}$ calc C, 49 4, H, 5 7, Cl, 4 3%)

Deacetylation of **10** afforded 6″-chloro-6′,4″,6″-trideoxyraffinose (**11**) as an amorphous, hygroscopic powder (67%), $[\alpha]_D$ +103° (*c* 0 25, methanol), which did not give a satisfactory analysis

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REFERENCES

1 L Hough, M A Salam, and E Tarelli, *Carbohydr Res*, 57 (1977) 97–101
2 B Helferich, *Ber*, 54 (1921) 1082–1089, B Helferich, A Lowa, W Nippe, and H Reidel, *ibid*, 56 (1923) 1083–1087 B Helferich, G Sproek, and E Besler, *ibid*, 58 (1925) 886–891
3 H J Jennings and J K N Jones, *Can J Chem*, 40 (1962) 1408–1414, 41 (1963) 1151–1159, 43 (1965) 2372–2386
4 A C Richardson, *Carbohydr Res*, 10 (1969) 395–402
5 G G Birch, C K Lee, and A C Richardson, *Carbohydr Res*, 36 (1974) 97–109
6 J M Ballard, L Hough, A C Richardson, and P H Fairclough, *J Chem Soc*, *Perkin Trans 1*, (1973) 1524–1528, and unpublished results (with S P Phadnis)
7 P L Durette, L Hough, and A C Richardson, *Carbohydr Res*, 31 (1973) 114–119
8 R S Bhatt L Hough and A C Richardson, *Carbohydr Res*, 49 (1976) 103–118
9 R G Edwards, L Hough, A C Richardson, and E Tarelli, *Carbohydr Res*, 35 (1974) 111–129
10 L Hough and S P Phadnis, *Nature (London)*, 263 (1976) 5580
11 A Allerhand and D Doddrell, *J Am Chem Soc*, 93 (1971) 2779–2781
12 A Allerhand and D Doddrell, *J Am Chem Soc*, 93 (1971) 2777–2779
13 L Hough, A K Palmer, and A C Richardson, *J Chem Soc*, *Perkin Trans 1*, (1972) 2513–2517
14 L Hough and J K N Jones, *Methods Carbohydr Chem*, 1 (1962) 21–31
15 H J Jennings, *Can J Chem*, 49 (1971) 1355–1359