A Convenient Method for *S*-Glycosidic Bond Formation. Synthesis of *p*-Iodophenyl 4'-Thiomaltotrioside and its 2",3"-Unsaturated Analogue

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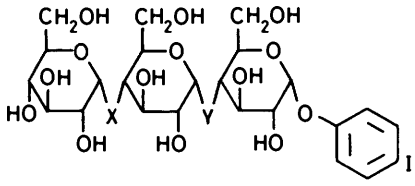
The axial trifluoromethanesulphonate group at C-4' of acylated galactopyranosylglucopyranoside (**11**) was substituted by sulphur nucleophiles: selective *S*-deacetylation and activation of peracetylated 1-thio-α-D-glucose (**12**) led to *p*-iodophenyl 4'-thiomaltotrioside derivative (**13**); substitution by potassium thioacetate and *S*-deacetylation afforded 4'-thiomaltoside (**17**) which gave, by condensation with acetylated 1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol, under acidic conditions, as a major product the 2",3"-unsaturated trisaccharide (**19**). The synthesis of compound (**2**), the sulphur positional isomer of (**1**), in 73% yield is also reported.

X-Ray analysis is one of the best procedures for the investigation and comprehension of interaction between two molecules, and also as an aid for designing new compounds of biological importance. For example, crystallographic data on enzyme–substrate complexes for lysozyme,[1] chymotrypsin,[2] and glycogen phosphorylase[3] were useful for understanding the mechanism of action or the specificity of these enzymes, and also for studies of substrate conformation[4] in the active site.

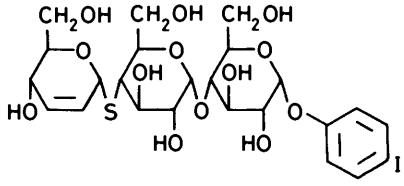
For porcine pancreatic α-amylase, in 1980, the first report of the use of substrate analogue derivatives for *X*-ray studies showed two binding sites, one in a crevice, the second one on the surface of the molecule.[5] Kinetic analyses, with small substrates, have shown that the catalytic site, probably the former, consists of several binding subsites.[6] The surface site is assumed to act only as a regulation or a storage function *in vivo* and it may be involved in allosteric control *in vitro*.

The present work deals with the synthesis of a new class of inhibitors labelled with a heavy atom suitable for visualizing the substrate orientation in both sites of the α-amylase crystal. These compounds were designed by the combination of our previous work on thiomalto-oligosaccharides[7] and of the inhibitory effect of several pseudo-oligosaccharides such as acarbose and its homologues.[8] These later compounds have been isolated from culture broth of micro-organisms or obtained by chemical synthesis[9] and it was claimed that the characteristic core-structure essential for inhibitory action is a trihydroxy(hydroxymethyl)cyclohexene unit linked by an allylic amino bond to the 4" position of a maltotriose residue. It was also reported[8] that the saturated compound obtained by catalytic hydrogenation of the double bond had no inhibitory effect against α-amylase.

Since acarbose may be seen as a pseudo-maltotetraose modified on its non-reducing residue, and since thioglycosides are known to be inhibitors of glycanases,[10] we synthesized the trisaccharide (1), its 2",3"-unsaturated analogue (**3**), and the isomer of (**1**), compound (**2**).



(**1**) X = S, Y = O
(**2**) X = O, Y = S



(**3**)

Results and Discussion

The general strategy, starting from the known 1,2,2',3,3',6-hexa-*O*-acetyl-β-maltose (**4**),[11] for building trisaccharides containing a sulphur atom on the non-reducing interglycosidic linkage, is as follows.

It was necessary, in the first step, to protect the 6'-position of the maltose residue (**4**). Preferential benzoylation was readily obtained in excellent yield using the new 1-(benzoyloxy)-benzotriazole procedure.[12] Inversion at the 4'-position of benzoate (**5**) was also achieved in good yield by displacement of the trifluoromethanesulphonate (triflate) group of compound (**6**) by nitrite ion, followed by its *in situ* hydrolysis,[13] and thus compound (**7**) was prepared in 37% overall yield.

A trichloroacetyl group was selected as a temporary blocking group for the 4'-OH group of (**7**); the glycosidation procedure, already developed for the synthesis of *p*-nitrophenyl galactopyranoside,[14] smoothly converted compound (**8**) into an α:β (2:1) anomeric mixture of *p*-iodophenyl glycosides (**9**) evaluated by ^{1}H n.m.r. spectroscopy.

Selective de-*O*-trichloroacetylation using a dichloromethane–methanol–pyridine solution[15] led to compound (**10**) in quantitative yield. The free hydroxy group of this compound was quantitatively esterified with trifluoromethanesulphonic anhydride in a mixture of dichloromethane–pyridine. In a previous work[16] a triflate group at the C-4 position of a galactosyl residue was substituted by the sodium salt of 1-thio-α-D-glucopyranose generated from peracetylated derivative (**12**).[17] In the present paper, we have developed a new method involving an *in situ* selective *S*-deacetylation and activation of compound (**12**) by cysteamine[18] in hexamethylphosphoramide

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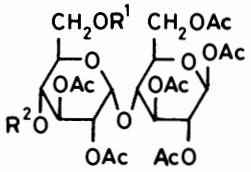
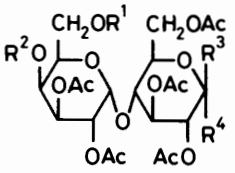
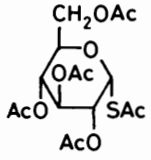


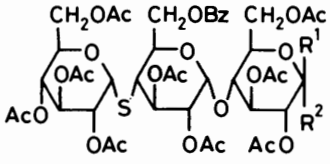
(4) $R^1 = R^2 = H$
(5) $R^1 = Bz$, $R^2 = H$
(6) $R^1 = Bz$, $R^2 = S(O)_2CF_3$



(7) $R^1 = Bz$, $R^2 = R^4 = H$, $R^3 = OAc$
(8) $R^1 = Bz$, $R^2 = C(O)CCl_3$, $R^3 = OAc$, $R^4 = H$
(9) $R^1 = Bz$, $R^2 = C(O)CCl_3$, $R^3, R^4 = OC_6H_4I\text{-}p$, H
(10) $R^1 = Bz$, $R^2 = H$, $R^3, R^4 = OC_6H_4I\text{-}p$, H
(11) $R^1 = Bz$, $R^2 = S(O)_2CF_3$, $R^3, R^4 = OC_6H_4I\text{-}p$, H



(12)

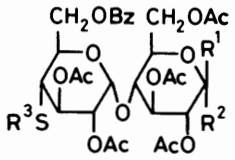


(13) $R^1 = H$, $R^2 = OC_6H_4I\text{-}p$
(14) $R^1 = OC_6H_4I\text{-}p$, $R^2 = H$

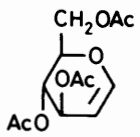
(HMPA)* in the presence of 1,4-dithioerythritol. Under these conditions, the triflate (**11**) reacted at room temperature in 2 h and the trisaccharides (**13**) and (**14**) were obtained in 69% yield. The anomeric mixture of the starting disaccharide residue was resolved at this step by careful column chromatography and led to compounds (**13**) and (**14**) in 45 and 19% yield respectively.

Displacement of the triflate group of disaccharide (**11**) by thioacetyl nucleophiles in tetrahydrofuran (THF) was also investigated. Tetrabutylammonium and potassium salts afforded the expected anomeric compounds (**15**) and (**16**), but it was found more convenient to use potassium thioacetate. Under the conditions described, (**15**) and its β-anomer (**16**) were obtained in 44 and 22% yield respectively. The method already described for the *S*-deacetylation of compound (**12**) allowed us to obtain readily the free-thiol compound (**17**). This procedure is a good alternative to the chlorophenylmercury(II) acetate–hydrogen sulphide method developed by Ferrier,[19] and augured well for a successful synthesis of higher thio-oligosaccharides.

* This activation is evident from the following experiment. The well known crystalline 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (D. Horton, *Methods Carbohydr. Chem.*, 1963, **2**, 433) was unable to substitute the triflate group of methyl 2,3,6-tri-*O*-benzoyl-4-*O*-trifluoromethylsulphonyl-α-D-galactopyranoside[16] in the absence of cysteamine. However, in the presence of 1.2 equiv. of this reagent, a methyl acylated 4-thiocellobioside[17] was obtained in 47% yield.



(15) $R^1 = H$, $R^2 = OC_6H_4I\text{-}p$, $R^3 = Ac$
(16) $R^1 = OC_6H_4I\text{-}p$, $R^2 = H$, $R^3 = Ac$
(17) $R^1 = R^3 = H$, $R^2 = OC_6H_4I\text{-}p$



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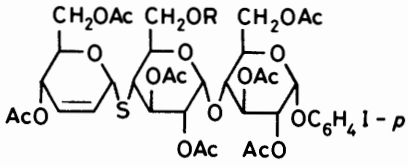
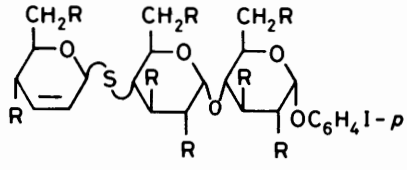
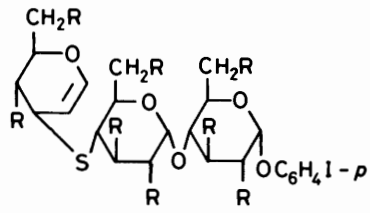


(19) R = Bz
(20) R = Ac

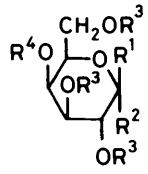


(21) R = OH
(22) R = OAc

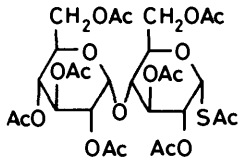


(23) R = OH
(24) R = OAc

2,3-Unsaturated glycosides can be obtained in a well known Lewis acid-catalysed rearrangement of glycals in the presence of nucleophiles. This transformation has been extensively studied by Ferrier's group[20] and others[21] and led as expected to the formation of the C-1-substituted derivatives in high yield when alcohols are used. However, with other nucleophiles the reaction products are usually a mixture of C-1- and C-3-substituted glycals due to reversible allylic rearrangement or to an attack at C-1 and C-3. These results can be rationalized by Pearson's hard-and-soft acid-and-base principles.[22] An alcohol binds to the hard carbocationic centre of the sugar molecule (*i.e.* C-1) and azide, thiol, and thiocyanate interact with the soft acid site (*i.e.* C-3) or lead to migration C-1 ⟶ C-3 since the hard–soft combination is destabilized.[23–25] In the present work, electron-withdrawing acetyl groups vicinal to the thiol in structure (**17**) should harden the soft sulphur atom which attacks preferentially the harder centre of the acetylated 1-enopyranose (**18**) to lead to the coupling compounds in 68% yield. In this mixture, the expected C-1″ axially substituted 2″,3″-



(25) R^1 = OAc, R^2 = H, R^3 = R^4 = Ac
(26) R^1 = H, R^2 = OC_6H_4I-*p*, R^3 = R^4 = Ac
(27) R^1 = OC_6H_4I-*p*, R^2 = H, R^3 = R^4 = Ac
(28) R^1 = R^3 = R^4 = H, R^2 = OC_6H_4I-*p*
(29) R^1 = R^4 = H, R^2 = OC_6H_4I-*p*, R^3 = Bz
(30) R^1 = H, R^2 = OC_6H_4I-*p*, R^3 = Bz, R^4 = $S(O)_2CF_3$



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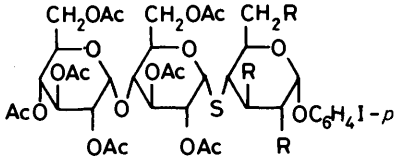

(32) R = OBz
(33) R = OAc

dideoxy-2″-enopyranosyl compound (**19**) is the major product isomer but its isolation was very difficult. Reverse-phase h.p.l.c. was used to purify (**3**) from (**21**) and (**23**) which were obtained in the proportions 5:1:1 after catalytic deacylation of compound (**19**) and its isomers. A further characterization of these compounds by ^{1}H n.m.r. spectroscopy was made through their conversion into their corresponding fully acetylated derivatives (**20**), (**22**), and (**24**).

The trisaccharide (**2**) was also obtained by a similar reaction pathway starting from penta-*O*-acetylgalactopyranose (**25**). Condensation with *p*-iodophenol led to the acetylated *p*-iodophenyl α-D-galactoside (**26**) and its β-anomer (**27**) in 53 and 35% yield respectively. Deacetylation of (**26**) led to compound (**28**), and selective benzoylation gave the expected 2,3,6-tri-*O*-benzoyl derivative (**29**) in quantitative yield when (benzoyloxy)benzotriazole was the acylating reagent. The free hydroxy group of this compound was quantitatively esterified with trifluoromethanesulphonic anhydride in a mixture of dichloromethane–pyridine. Displacement of the triflate group of (**30**) by peracetylated α-thiomaltose (**31**) under the previously described conditions gave the trisaccharide (**32**) in 73% yield.

Characterization of all the protected compounds was performed by ^{1}H and ^{13}C n.m.r. spectroscopy and by ^{13}C n.m.r. spectroscopy for the free compounds (**1**), (**2**), (**3**), (**21**), and (**23**) obtained by catalytic deacetylation of the acetyl derivatives.

The utility of these compounds for *X*-ray diffraction studies and chemical modification experiments of α-amylases will be reported elsewhere.

Experimental

Usual work-up means: after dilution with dichloromethane, the organic phase was successively washed with ice-cold aqueous solutions of potassium hydrogen sulphate (10%) and saturated sodium hydrogen carbonate, then with ice-cold water. Aqueous washings were then back-extracted with dichloromethane. Solutions were dried (Na_2SO_4), and evaporated under reduced pressure at temperatures below 45 °C. T.l.c. was performed on silica gel (Merck F 254, Merck, Darmstadt, Germany). Preparative chromatography and flash-chromatography used Kieselgel 60 (70—230 Mesh) and Kieselgel 60 (230—400 Mesh) respectively. Optical rotations were determined with a Perkin Elmer polarimeter at 25 °C. The ^{1}H n.m.r. spectra (Table) were recorded at 300 MHz with a Bruker AM 300. Assignments were confirmed by double irradiation or a 2D COSY program. The ^{13}C n.m.r. spectra were recorded at 25.18 MHz—on a Bruker WP 100 (unless otherwise mentioned). Light petroleum refers to the fraction boiling in the range 40—70 °C.

The following eluant systems were used (v/v): (A) ethyl acetate–light petroleum (1:1.5), (B) ethyl acetate–light petroleum (1:3), (C) ethyl acetate–light petroleum (1:1), (D) ethyl acetate–light petroleum (1:2), (E) diethyl ether, (F) diethyl ether–light petroleum (4:1), (G) diethyl ether–hexane (2:1), (H) dichloromethane–diethyl ether (9:1), (I) diethyl ether–toluene (9:2).

1,2,3,6-*Tetra*-O-*acetyl*-4-O-(2,3-*di*-O-*acetyl*-6-O-*benzoyl*-α-D-*glucopyranosyl*)-β-D-*glucopyranose* (**5**).—To a stirred solution of 1,2,2′,3,3′,6-hexa-*O*-acetyl-β-maltose[11] (**4**) (8.34 g, 14.0 mmol) and 1-(benzoyloxy)benzotriazole[12] (4.08 g, 17.0 mmol) in dichloromethane (70 ml) was added triethylamine (2.95 ml, 21.3 mmol). The reaction mixture was stirred at room temperature for 24 h, diluted with dichloromethane (100 ml), washed successively with ice-cold saturated aqueous sodium hydrogen carbonate and water, dried, and evaporated. Purification of the residue by flash chromatography using eluant A gave the expected *product* (**5**) as an oil (7.2 g, 73%) (Found: C, 53.25; H, 5.7. $C_{31}H_{38}O_{18}$ requires C, 53.29; H, 5.48%); $[\alpha]_D^{25}$ +47° (*c* 0.58 in $CHCl_3$); δ_C (75 MHz; $CDCl_3$) 91.5 (C-1) and 96.1 (C-1′).

1,2,3,6-*Tetra*-O-*acetyl*-4-O-(2,3-*di*-O-*acetyl*-6-O-*benzoyl*-α-D-*galactopyranosyl*)-β-D-*glucopyranose* (**7**).—To an ice-cold solution of compound (**5**) (10.75 g, 15.4 mmol) in dichloromethane–pyridine (15:1; 160 ml) was added trifluoromethanesulphonic anhydride (5.1 ml, 30.8 mmol). After 30 min at 0 °C, then 1 h at room temperature, t.l.c. (solvent A) showed complete conversion of the starting material (**5**) into the more mobile triflate (**6**). Dilution of the reaction mixture with dichloromethane (250 ml) followed by the usual work-up led, after evaporation, to an oil (12.75 g, 100%), which was used without purification and further characterization in the next step.

To a solution of the above triflate (**6**) (12.75 g, 15.4 mmol) in DMF (120 ml) was added sodium nitrite (3.18 g, 46.1 mmol); after 3 h at room temperature, the mixture was evaporated, the residue was mixed with dichloromethane, the suspension was filtered, and the filtrate was evaporated. *Compound* (**7**) was isolated by flash chromatography (eluant A) as an oil (6.03 g, 56%), and crystallization in ethanol gave an analytical sample (5.5 g, 51%), m.p. 169—170 °C (Found: C, 53.1; H, 5.6. $C_{31}H_{38}O_{18}$ requires C, 53.29; H, 5.48%); $[\alpha]_D^{25}$ +75° (*c* 0.7 in $CHCl_3$); δ_C (75 MHz; $CDCl_3$) 91.5 (C-1) and 96.5 (C-1′).

1,2,3-6-*Tetra*-O-*acetyl*-4-O-(2,3-*di*-O-*acetyl*-6-O-*benzoyl*-4-O-*trichloroacetyl*-α-D-*galactopyranosyl*)-β-D-*glucopyranose* (**8**).—To a solution of compound (**7**) (5.0 g, 7.2 mmol) in dichloromethane–pyridine (12:1; 65 ml) cooled to 0 °C was added trichloroacetyl chloride (3.2 ml, 28.6 mmol). After 30 min

at 0 °C, then 3 h at room temperature, t.l.c. (solvent A) showed complete conversion of the starting material into the more mobile product (**8**). Extraction with dichloromethane (200 ml) followed by the usual work-up led, after evaporation, to an oil, which was crystallized from ether to give *trichloroacetate* (**8**) (5.8 g, 97%), m.p. 123 °C (Found: C, 46.9; H, 4.4; Cl, 12.4. $C_{33}H_{37}Cl_3O_{19}$ requires C, 46.96; H, 4.42; Cl, 12.60%); $[\alpha]_D^{25}$ + 46° (*c* 0.81 in $CHCl_3$); δ_C (75 MHz; $CDCl_3$) 91.5 (C-1) and 96.4 (C-1′).

p-*Iodophenyl* 2,3,6-*Tri*-O-*acetyl*-4-O-(2,3-*di*-O-*acetyl*-6-O-*benzoyl*-4-O-*trichloroacetyl*-α-D-*galactopyranosyl*)-D-*gluco*-*pyranoside* (**9**).—A solution of compound (**8**) (3.0 g, 3.5 mmol), *p*-iodophenol (1.19 g, 5.4 mmol), and tin tetrachloride (1.78 ml) was stirred at room temperature for 90 min in alcohol-free chloroform–nitromethane (1:1; 36 ml). The solution was poured into ice-cold aqueous sodium hydrogen carbonate, then diluted with dichloromethane (150 ml). After filtration through Celite the precipitate was washed with dichloromethane and the organic phase was rapidly washed with ice-water, dried, and evaporated to give a syrup. Flash-chromatography using eluant B gave a mixture (isolated yield 2.4 g, 67%) of three products. Crystallization of the mixture in methanol gave the two expected anomers (**9**) (1.95 g, 55%) in the anomeric ratio 2:1 (^{1}H n.m.r. evaluation) (Found: C, 44.3; H, 4.0; I, 11.9. $C_{37}H_{38}Cl_3IO_{18}$ requires C, 44.26; H, 3.81; I, 12.64%). The third compound, which has not been identified, remained in the mother liquors.

p-*Iodophenyl* 2,3,6-*Tri*-O-*acetyl*-4-O-[2,3-*di*-O-*acetyl*-6-O-*benzoyl*-4-S-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-4-*thio*-α-D-*glucopyranosyl*]-α-D-*glucopyranoside* (**13**).—A solution of crude compound (**9**) (2.09 g, 2.1 mmol) in dichloromethane–methanol–pyridine (10:1:1) was stirred at room temperature for 24 h. T.l.c. (solvent A) showed complete conversion of the starting material (**9**) into the less mobile compound (**10**). The solution was evaporated and co-evaporated with toluene to give (**10**) as an oil (1.65 g, 100%), which was used without further purification in the next step.

Compound (**10**) (1..65 g, 1.9 mmol) was triflated with

Table. ^{1}H N.m.r. data (δ_H) for ring protons of the acylated derivatives in deuteriochloroform (*J*-values in Hz)[a,b]

	Compound							
Proton	(**5**)	(**7**)	(**8**)	(**13**)	(**15**)	(**17**)	(**19**)	(**20**)
1-H	5.75 d ($J_{1,2}$ 9.0)	5.73 d ($J_{1,2}$ 8.0)	5.73 d ($J_{1,2}$ 8.0)	5.56 d ($J_{1,2}$ 3.7)	5.57 d ($J_{1,2}$ 3.5)	5.57 d ($J_{1,2}$ 3.5)	5.57 d ($J_{1,2}$ 3.7)	5.57 d ($J_{1,2}$ 3.7)
2-H	4.96 dd ($J_{2,3}$ 10.0)	4.97 dd ($J_{2,3}$ 9.5)	4.97 dd ($J_{2,3}$ 9.0)	4.87 dd ($J_{2,3}$ 10.0)	4.88 ddb ($J_{2,3}$ 9.0)	4.88 dd ($J_{2,3}$ 10.0)	4.87 dd ($J_{2,3}$ 10.0)	4.90 dd ($J_{2,3}$ 10.0)
3-H	5.26 t ($J_{3,4}$ 10.0)	5.28 dd ($J_{3,4}$ 8.5)	5.29 t ($J_{3,4}$ 9.0)	5.69 dd ($J_{3,4}$ 8.0)	5.70 tb ($J_{3,4}$ 9.0)	5.70 dd ($J_{3,4}$ 8.0)	5.7 m	5.70 dd ($J_{3,4}$ 8.0)
4-H	3.61 t ($J_{4,5}$ 10.0)	4.04 dd ($J_{4,5}$ 10.0)	4.05 dd ($J_{4,5}$ 8.5)	4.0 m	4.0 m	4.0 m	3.98 t ($J_{4,5}$ 10.0)	3.98 dd ($J_{4,5}$ 10.0)
5-H	3.87 td ($J_{5,6a}$ 2.5)	3.80 o ($J_{5,6a}$ 4.5)	3.80 o ($J_{5,6a}$ 4.5)	4.2 m	4.2 m	4.0 m	4.2* m	4.1* m
6-H_a	4.46 dd ($J_{6a,6b}$ 12.5)	4.18 dd ($J_{6a,6b}$ 12.5)	4.17 dd ($J_{6a,6b}$ 12.5)	4.73* dd ($J_{5,6a}$ 3.5, $J_{6a,6b}$ 12.0)	4.0* m	4.73* dd ($J_{5,6a}$ 4.0, $J_{6a,6b}$ 12.0)	4.30* dd ($J_{5,6a}$ 2.0, $J_{6a,6b}$ 11.0)	4.56 dd ($J_{5,6a}$ 2.5, $J_{6a,6b}$ 12.0)
6-H_b	4.77 dd ($J_{5,6b}$ 3.5)	4.51 dd ($J_{5,6b}$ 3.5)	4.54 dd ($J_{5,6b}$ 2.5)	4.56* dd ($J_{5,6b}$ 5.0)	4.5* m	4.64 dd ($J_{5,6b}$ 3.0)	4.2* m	4.35 dd ($J_{5,6b}$ 4.0)
1′-H	5.36 d ($J_{1,2}$ 4.5)	5.44 d ($J_{1,2}$ 3.5)	5.51 d ($J_{1,2}$ 4.0)	5.36 d ($J_{1,2}$ 3.8)	5.45 d ($J_{1,2}$ 4.0)	5.42 d ($J_{1,2}$ 3.5)	5.38 d ($J_{1,2}$ 3.8)	5.39 d ($J_{1,2}$ 4.0)
2′-H	4.80 dd ($J_{2,3}$ 10.0)	5.28 dd ($J_{2,3}$ 11.0)	5.20 dd ($J_{2,3}$ 11.0)	4.74 dd ($J_{2,3}$ 10.5)	4.88 ddb ($J_{2,3}$ 10.0)	4.81 dd ($J_{2,3}$ 10.5)	4.80 dd ($J_{2,3}$ 11.0)	4.78 dd ($J_{2,3}$ 10.0)
3′-H	5.29 t ($J_{3,4}$ 10.0)	5.22 dd ($J_{3,4}$ 2.5)	5.40 dd ($J_{3,4}$ 3.0)	5.45 t ($J_{3,4}$ 10.5)	5.45 t ($J_{3,4}$ 10.0)	5.21 t ($J_{3,4}$ 10.5	5.42 t ($J_{3,4}$ 11.0)	5.39 t ($J_{3,4}$ 10.0)
4′-H	4.03 dd ($J_{4,5}$ 9.0)	4.1 m	5.63 dd ($J_{4,5}$ 1.0)	3.13 t ($J_{4,5}$ 10.5)	3.79 td ($J_{4,5}$ 11.0)	2.98 q ($J_{4,5}$ 10.5)	3.15 t ($J_{4,5}$ 11.0)	3.04 t ($J_{4,5}$ 10.0)
5′-H	3.83 o ($J_{5,6a}$ 2.7)	4.1 m	4.4 m	4.1 m	4.2 m	4.0 m	4.1* m	4.3* m
6′-H_a	4.20 dd ($J_{6a,6b}$ 12.0)	4.32 dd ($J_{5,6a}$ 5.5, ($J_{6a,6b}$ 12.5)	4.17 dd ($J_{5,6a}$ 4.5, $J_{6a,6b}$ 12.5)	4.38* dd ($J_{5,6a}$ 2.2, $J_{6a,6b}$ 12.0)	4.5* m	4.44* dd ($J_{5,6a}$ 4.5, $J_{6a,6b}$ 12.0)	4.2* m	4.3* m
6′-H_b	4.51 dd ($J_{5,6b}$ 4.5)	4.67 dd ($J_{5,6b}$ 7.5)	4.4 m	4.2* m	4.5* m	4.15 dd ($J_{5,6b}$ 3.5)	4.2* m	4.3* m
1″-H				5.92 d ($J_{1,2}$ 6.0)			5.74 sb	5.7 m
2″-H				4.97 dd ($J_{2,3}$ 10.5)			5.8 m	5.8 m
3″-H				5.24 dd ($J_{3,4}$ 10.0)			5.8 m	5.8 m
4″-H				5.03 t ($J_{4,5}$ 10.0)			4.8 m	5.33 dd ($J_{3,4}$ 2.0, $J_{4,5}$ 9.5)
5″-H				4.2 m			4.2* m	3.9* m
6″-H_a				4.0* m			4.0* m	4.3*
6″-H_b				4.2* m			4.2* m	4.3* m

(Table continued overleaf)

Table (*continued*)

Proton	Compound (22)	(24)	(26)	(27)	(29)	(32)	(33)
1-H	5.60 d ($J_{1,2}$ 3.4)	5.57 d ($J_{1,2}$ 3.6)	5.74 d ($J_{1,2}$ 3.5)	4.99 d ($J_{1,2}$ 8.0)	5.95 d ($J_{1,2}$ 3.5)	5.90 d ($J_{1,2}$ 3.5)	5.62 d ($J_{1,2}$ 4.0)
2-H	4.91 dd ($J_{2,3}$ 10.5)	4.89 dd ($J_{2,3}$ 10.0)	5.27 dd ($J_{2,3}$ 10.5)	5.45 dd ($J_{2,3}$ 10.5)	5.86 dd ($J_{2,3}$ 11.0)	5.27 dd ($J_{2,3}$ 10.0)	4.91 dd ($J_{2,3}$ 10.0)
3-H	5.70 dd ($J_{3,4}$ 9.0)	5.69 dd ($J_{3,4}$ 8.0)	5.54 dd ($J_{3,4}$ 3.5)	5.08 dd ($J_{3,4}$ 3.5)	5.94 dd ($J_{3,4}$ 3.0)	6.23 tb ($J_{3,4}$ 10.0)	5.71 t ($J_{3,4}$ 10.0)
4-H	3.98 t ($J_{4,5}$ 10.0)	4.03 t ($J_{4,5}$ 8.0)	5.52 dd ($J_{4,5}$ 1.0)	5.44 dd ($J_{4,5}$ 1.0)	4.5* m	3.33 t ($J_{4,5}$ 11.0)	3.10 t ($J_{4,5}$ 10.0)
5-H	4.1* m	4.26 dq ($J_{5,6a}$ 2.5)	4.29 tb ($J_{5,6a}$ 6.0)	4.04 o ($J_{5,6a}$ 7.0)	4.6* m	4.30 m	4.0*
6-H_a	4.5* m	4.45 dd ($J_{6a,6b}$ 12.0)	4.12 dd ($J_{6a,6b}$ 11.5)	4.20 dd ($J_{6a,6b}$ 11.0)	4.6* m	4.90 dd ($J_{6a,6b}$ 12.0, $J_{5,6a}$ 2.0)	4.6* m
6-H_b	4.5* m	4.4 m*	4.04 dd ($J_{6b,5}$ 7.0)	4.16 dd ($J_{6b,5}$ 6.0)	4.6* m	4.64 dd ($J_{5,6b}$ 7.5)	4.55* m
1′-H	5.38 d ($J_{1,2}$ 3.9)	5.37 d ($J_{1,2}$ 4.0)				5.66 d ($J_{1,2}$ 6.0)	5.71 d ($J_{1,2}$ 6.0)
2′-H	4.83 dd ($J_{2,3}$ 10.0)	5.10 dd ($J_{2,3}$ 10.0)				4.79 dd ($J_{2,3}$ 9.0)	4.86 dd ($J_{2,3}$ 10.0)
3′-H	5.36 dd ($J_{3,4}$ 11.0)	5.19 dd ($J_{3,4}$ 11.0)				5.12 dd ($J_{3,4}$ 7.5)	5.28 dd ($J_{3,4}$ 9.0)
4′-H	2.90 t ($J_{4,5}$ 11.0)	2.88 t ($J_{4,5}$ 11.0)				3.83 dd ($J_{4,5}$ 11.5)	4.30 t
5′-H	4.1* m	3.8 m				4.30 m	4.0* m
6′-H_a	4.2* m	4.4 m*				4.51 dd ($J_{6a,6b}$ 11.5, $J_{5,6a}$ 1.0)	4.20* m
6′-H_b	4.5* m	4.4 m*				4.30 m	4.20* m
1″-H	5.58 sb	6.38 db ($J_{1,2}$ 5.8)				5.33 d ($J_{1,2}$ 4.0)	5.40 d ($J_{1,2}$ 4.0)
2″-H	5.90 dt ($J_{1,2}$ 2.2. $J_{2,3}$ 10.2)	4.80 t ($J_{2,3}$ 6.0. $J_{3,4}$ 6.0)				4.86 dd ($J_{2,3}$ 10.0)	4.87 dd ($J_{2,3}$ 10.0)
3″-H	5.70 dd ($J_{3,4}$ 2.0)	3.80 m				5.34 dd ($J_{3,4}$ 10.0)	5.08 t ($J_{3,4}$ 10.0)
4″-H	5.36 m	4.78 dd ($J_{4,5}$ 11.0)				5.05 t ($J_{4,5}$ 10.0)	5.38 dd ($J_{4,5}$ 10.5)
5″-H	3.80 q	4.1 m*				3.96 m	4.0* m
6″-H_a	4.2* m	4.1 m*				4.23 dd ($J_{6a,6b}$ 12.5, $J_{6a,5}$ 4.0)	4.20* m
6″-H_b	4.2* m	4.1 m*				4.06 dd ($J_{6b,5}$ 2.5)	4.20* m

[a] The primed numbers refer to the protons of the penultimate (central) residue for trisaccharides or of the terminal non-reducing unit for disaccharides; double-primed for the protons of the terminal unit of trisaccharides. [b] Abbreviations: b, broad signal; o, octet. * The assignments may be reversed in the same column.

trifluoromethanesulphonic anhydride (0.64 ml, 3.8 mmol) in a dichloromethane–pyridine mixture. Extraction with dichloromethane (150 ml) followed by the usual work-up gave, after evaporation, the syrupy triflate (**11**) (1.9 g, 100%), which was used without further purification in the next step.

To a solution of the crude triflate (**11**) in HMPA (30 ml) were added successively 2,3,4,6-tetra-*O*-acetyl-1-*S*-acetyl-1-thio-α-D-glucopyranose [16] (**12**) (1.27 g, 3.1 mmol), 1,4-dithioerythritol (574 mg, 3.7 mmol), and cysteamine (287 mg, 3.7 mmol). The mixture was stirred at room temperature for 2 h, then poured into ice–water. The solid was isolated by filtration through a bed of Celite, washed with water, then dissolved in dichloromethane and extracted with ice-cold water. Flash-chromatography with eluant A gave the expected compounds (**13**) and (**14**) (1.72 g, 69%). The two anomers were resolved by three careful successive column chromatographic separations with eluant C to yield (**13**) (1.12 g, 45%) and its β anomer (**14**) (484 mg, 19%). Crystallization of (**13**) from ether (896 mg, 36%) gave an analytical sample m.p. 118—120 °C (Found: C, 48.6; H, 4.9; I, 10.4; S, 3.2. $C_{49}H_{57}IO_{25}S$ requires C, 48.84; H, 4.77; I, 10.53; S, 2.66%); $[\alpha]_D^{25}$ +196° (*c* 0.9 in $CHCl_3$); δ_C (75 MHz; $CDCl_3$) 94.4 (C-1), 96.2 (C-1′), 82.4 (C-1″), 73.3 (C-4), and 43.9 (C-4′).

p-*Iodophenyl* 2,3,6-*Tri*-O-*acetyl*-4-O-(2,3-*di*-O-*acetyl*-4-5-*acetyl*-6-O-*benzoyl*-4-*thio*-α-D-*glucopyranosyl*)-α-D-*glucopyranoside* (**15**).—To a solution of the crude triflate (**11**) (1.9 g, 1.9 mmol) in freshly distilled THF (30 ml) was added potassium thioacetate (656 mg, 5.7 mmol) and the solution was stirred for 24 h at room temperature. Then the solution was filtered, the precipitate was washed with dichloromethane, and the filtrate was extracted with ice-cold water, dried, and evaporated to give

the crude product (**15**) and its anomer (**16**). The two anomers were resolved by three careful chromatographic separations in eluant A to yield the *title compound* (**15**) (782 mg, 44%) (Found: C, 48.7; H, 4.6; I, 13.7; S, 3.7. $C_{37}H_{41}IO_{17}S$ requires C, 48.48; H, 4.51; I, 13.84; S, 3.49%); $[\alpha]_D^{25}$ +165° (*c* 0.5 in $CHCl_3$); δ_C ($CDCl_3$) 94.3 (C-1), 96.1 (C-1′), and 44.3 (C-4′).

The β-anomer (**16**) was also isolated (392 mg, 22%).

p-*Iodophenyl* 2,3,6-*Tri*-O-*acetyl*-4-O-(2,3-*di*-O-*acetyl*-6-O-*benzoyl*-4-*thio*-α-D-*glucopyranosyl*)-α-D-*glucopyranoside* (**17**).—To a solution of compound (**15**) (673 mg, 0.73 mmol) in HMPA (10 ml) were added successively 1,4-dithioerythritol (113 mg, 0.73 mmol) and cysteamine (68 mg, 0.87 mmol). The solution was stirred at room temperature for 40 mn and then ice was added to the mixture. The solid was isolated by filtration through a bed of Celite, washed with water, then dissolved in dichloromethane; this solution was then extracted with ice-cold water, dried, and evaporated. The resulting oil was straightway filtered through a silica gel column with diethyl ether as eluant to give the crude product (**17**) (615 mg, 94%), which was then purified by flash chromatography using eluant A to yield compound (**17**) (494 mg, 75%), which could be used without further purification in the next condensation step. An *analytical sample* was obtained by two successive column chromatographic separations using eluants D and E (Found: C, 48.0; H, 4.6; I, 14.6; S, 3.7. $C_{35}H_{39}IO_{16}S$ requires C, 48.06; H, 4.49; I, 14.51; S, 3.66%); $[\alpha]_D^{25}$ +136° (*c* 0.7 in $CHCl_3$); δ_C($CDCl_3$) 94.3 (C-1), 96.2 (C-1′), and 40.8 (C-4).

p-*Iodophenyl* 4-O-[4-S-(2,3-*Dideoxy*-α-D-erythro-*hex*-2-*enopyranosyl*)-4-*thio*-α-D-*glucopyranosyl*]-α-D-*glucopyranoside* (**3**).—A mixture of triacetyl-D-enopyranose (**18**) (95 mg, 0.35 mmol), compound (**17**) (203 mg, 0.23 mmol), and $ZnBr_2$ (32 mg, 0.14 mmol) in toluene (5 ml) was stirred for 2 h at 65 °C. The solution was diluted with dichloromethane (25 ml), washed successively with ice-cold saturated aqueous hydrogen carbonate and water, dried, and evaporated to give a syrupy compound (310 mg). Chromatography on two successive silica gel columns with eluant F, led to a t.l.c.-homogeneous compound (171 mg, 68%) which was in fact the expected trisaccharide (**19**) contaminated with its anomers. However, pure compound (**19**) (10 mg) was isolated and was analysed by ^1H n.m.r. spectroscopy. Since resolution of this mixture of anomers by classical chromatographic techniques failed, compound (**19**) was not further characterized.

Compound (**19**) (144 mg, 0.13 mmol) was dissolved in methanol (10 ml) containing 1M-sodium methoxide (0.4 ml). After one night at room temperature, the reaction mixture was neutralized with Amberlite [H^+] to give a 5:1:1 mixture of three compounds which could be separated by h.p.l.c. on a reverse-phase C_{18} column (Waters Associates, Milford MA 01757) using MeOH–water (60:40) as eluant to yield the *title compound* (**3**) (62 mg, 68%). After evaporation, the freeze-dried compound was analytically pure (Found: C, 40.4; H, 5.1; I, 18.2; S, 4.4. $C_{24}H_{33}IO_{13}S\cdot1.5\,H_2O$ requires C, 40.28; H, 5.07; I, 17.73; S, 4.48%); $[\alpha]_D^{25}$ +214° (*c* 0.7 in MeOH); δ_C (75 MHz; D_2O) 98.0 (C-1), 102.1 (C-1′), 86.9 (C-1″), 127.6 and 132.0 (C-2″ and C-3″), and 48.6 (C-4′).

The two minor isomers (**21**) and (**23**) were also isolated, (12 mg, 13%) and (11 mg, 12%) respectively.

For (**21**), δ_C (75 MHz; D_2O) 97.5 (C-1), 101.1 (C-1′), 81.0 (C-1″), 129.0 and 132.3 (C-2″ and C-3″), and 47.6 (C-4′).

For (**23**), δ_C (75 MHz; D_2O) 98.0 (C-1), 100.4 (C-1′), 144.9 (C-1″), 102.1 (C-2″), 50.2 (C-3″), and 45.9 (C-4′).

p-*Iodophenyl* 2,3,6-*Tri*-O-*acetyl*-4-O-[2,3,6-*tri*-O-*acetyl*-4-S-(4,6-*di*-O-*acetyl*-2,3-*dideoxy*-α-D-erythro-*hex*-2-*enopyranosyl*)-4-*thio*-α-D-*glucopyranosyl*]-α-D-*glucopyranoside* (**20**).—Acetylation of compound (**3**) under the previously described conditions led to the *title compound* (**20**) in quantitative yield. An analytical sample was obtained after filtration through a small silica gel column with eluant E (Found: C, 47.0; H, 4.9; I, 12.3; S, 3.6. $C_{40}H_{49}IO_{21}S$ requires C, 46.88; H, 4.82; I, 12.38; S, 3.13%); $[\alpha]_D^{25}$ +181° (*c* 1.0 in $CHCl_3$); δ_C (75 MHz; $CDCl_3$) 94.4 (C-1), 96.3 (C-1′), 81.3 (C-1″), 127.8 and 128.3 (C-2″ and C-3″), and 46.9 (C-4′).

Acetylation of compound (**21**) as already described led to the isomeric octa-acetate (**22**), δ_C($CDCl_3$) 94.2 (C-1), 96.2 (C-1′), 77.7 (C-1″), 128.3 and 128.9 (C-2″ and C-3″), and 45.5 (C-4′).

Acetylation of compound (**23**) led to octa-acetate (**24**), δ_C($CDCl_3$) 94.3 (C-1), 96.3 (C-1′), 144.7 (C-1″), 98.4 (C-2″), 40.6 (C-3″), 46.3 (C-4′).

p-*Iodophenyl* 4-O-[4-S-(α-D-*Glucopyranosyl*)-4-*thio*-α-D-*glucopyranosyl*]-α-D-*glucopyranoside* (**1**).—Compound (**13**) (100 mg, 0.08 mmol) was suspended in methanol (10 ml) containing 1M-sodium methoxide (0.2 ml). After the mixture had been stirred overnight neutralization with Amberlite [H^+] led to a residue, which was crystallized in aqueous MeOH to give the *product* (**1**) m.p. 171—173 °C (51 mg, 85%) (Found: C, 39.6; H, 4.9; I, 16.8; S, 4.1. $C_{24}H_{35}IO_{15}S$ requires C, 39.44; H, 4.95; I, 17.33; S, 4.38%); $[\alpha]_D^{25}$ +225° (*c* 0.13 in water); δ_C(75 MHz; D_2O) 97.8 (C-1), 101.4 (C-1′), 87.2 (C-1″), 78.7 (C-4), and 47.9 (C-4″).

p-*Iodophenyl* 2,3,4,6-*Tetra*-O-*acetyl*-α-D-*galactopyranoside* (**26**).—A solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose (**25**) (2 g, 5.0 mmol), *p*-iodophenol (1.6 g, 7.2 mmol), and tin tetrachloride (1.8 ml) was stirred at 60 °C for 20 h in freshly distilled chloroform (10 ml). The solution was poured into ice-cold aqueous sodium hydrogen carbonate. After filtration through Celite, the precipitate was dissolved in dichloromethane and the solution was washed with ice–water. The expected *compound* (**26**) (1.5 g, 53%) was isolated by chromatography on a column of silica gel (eluant G). Crystallization from diethyl ether–hexane gave an analytical sample (1.4 g, 49%), m.p. 115 °C (Found: C, 43.5; H, 4.5; I, 23.1. $C_{20}H_{23}IO_{10}$ requires C, 43.63; H, 4.21; I, 23.07%); $[\alpha]_D^{25}$ +163° (*c* 0.8 in $CHCl_3$); δ_C($CDCl_3$) 94.9 (C-1).

p-Iodophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**27**) was then eluted from the column (1.0 g, 35%), δ_C($CDCl_3$) 99.5 (C-1).

p-*Iodophenyl* α-D-*Galactopyranoside* (**28**).—Compound (**26**) (1.3 g) was suspended in methanol (100 ml) containing 1M-sodium methoxide (1 ml). After 12 h, neutralization with Amberlite [H^+] led to the *deprotected glycoside* (**28**) in quantitative yield (910 mg), m.p. 137—140 °C (from Pr^iOH) (Found: C, 37.5; H, 3.9; I, 31.4. $C_{12}H_{15}IO_6$ requires C, 37.71; H, 3.96; I, 33.21%); $[\alpha]_D^{25}$ +226° (*c* 0.76 in MeOH).

p-*Iodophenyl* 2,3,6-*Tri*-O-*benzoyl*-α-D-*galactopyranoside* (**29**).—Compound (**28**) (764 mg, 2.0 mmol) was stirred at room temperature for 2 days with 1-(benzoyloxy)benzotriazole (1.74 g, 7.2 mmol) and triethylamine (1.1 ml, 8 mmol) in dichloromethane (15 ml). Work-up as already described for compound (**5**) afforded the *tri*-O-*benzoyl derivative* (**29**) in almost quantitative yield after crystallization from ethanol (1.75 g), m.p. 178—181 °C. T.l.c. examination (solvent H) shows a slight contamination with a slow moving compound. An analytical sample was obtained on a silica gel column with the same solvent, m.p. 181—182 °C (from EtOH) (Found: C, 56.8; H, 3.9; I, 18.25. $C_{33}H_{27}IO_9$ requires C, 57.07; H, 3.92; I, 18.27%); $[\alpha]_D^{25}$ +131° (*c* 0.51 in MeOH); δ_C (CD_3OH) 95.0 (C-1).

p-*Iodophenyl* 2,3,6-*Tri*-O-*benzoyl*-4-S-[4-O-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-2,3,6-*tri*-O-*acetyl*-α-D-*glucopyrano-*

syl]-4-*thio*-α-D-*glucopyranoside* (**32**).—The crude glycoside (**29**) (347 mg, 0.5 mmol) was triflated with trifluoromethanesulphonic anhydride (0.2 ml) in a dichloromethane–pyridine mixture (4 ml; 1:1). After usual work-up, the triflate (**30**), without characterization, was condensed as already described for the reaction of compound (**11**) in HMPA (5 ml) with 2,3,6-tri-*O*-acetyl-1-*S*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-thio-α-D-glucopyranose (**31**) (420 mg, 0.6 mmol) in the presence of 1,4-dithioerythritol (116 mg) and cysteamine (58 mg). The mixture was stirred at room temperature for 3 h, then poured into ice–water. The solid was isolated by filtration through a bed of Celite, washed with water, then dissolved in dichloromethane, and the solution was extracted with ice-cold water. T.l.c. examination (solvent I) showed only one major spot with minor contaminants. Purification on a silica gel column with the same solvent afforded pure *title compound* (**32**) (490 mg, 73%) (Found: C, 53.2; H, 4.6; I, 9.2; S, 2.4. $C_{59}H_{61}IO_{25}S$ requires C, 53.32; H, 4.63; I, 9.54; S, 2.41%); $[\alpha]_D^{25}$ +196° (*c* 0.13 in $CHCl_3$); δ_C($CDCl_3$) 94.6 (C-1), 83.8 (C-1′), 96.1 (C-1″), and 46.2 (C-4).

p-*Iodophenyl* 4-*S*-[4-*O*-(α-D-*Glucopyranosyl*)-α-D-*glucopyranosyl*]-4-*thio*-α-D-*glucopyranoside* (**2**).—Compound (**32**) (200 mg) was de-*O*-acylated by 1M-sodium methoxide (0.5 ml) in methanol (20 ml), in quantitative yield (Found: C, 39.1; H, 5.15; I, 16.3; S, 4.5. $C_{24}H_{35}IO_{14}S{\cdot}H_2O$ requires C, 38.96; H, 5.03; I, 17.12; S, 4.32%); $[\alpha]_D^{25}$ +279° (*c* 0.6 in MeOH); δ_C (75 MHz; D_2O) 97.7 (C-1), 86.9 (C-1′), 100.6 (C-1″), 47.7 (C-4), and 78.2 (C′-4).

p-*Iodophenyl* 2,3,6-*Tri*-O-*acetyl*-4-S-[4-O-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-2,3,6-*tri*-O-*acetyl*-α-D-*glucopyranosyl*]-4-*thio*-α-D-*glucopyranoside* (**33**).—Acetylation of compound (**2**) led in quantitative yield to the expected *derivative* (**33**) (Found: C, 46.4; H, 4.9; S, 2.7; I, 10.8. $C_{44}H_{55}IO_{25}S$ requires C, 46.24; H, 4.85; S, 2.80; I, 11.10%); $[\alpha]_D^{25}$ +215° (*c* 0.8 in $CHCl_3$); δ_C($CDCl_3$) 94.3 (C-1), 82.4 (C-1′), 95.6 (C-1″), and 44.1 (C-4).

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