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Syntheses of hepta-, hexa-, and penta-pivalates of trehalose by selective pivaloylation*

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ABSTRACT

The order of esterification of the eight hydroxyl groups of trehalose with pivaloyl chloride is HO-6,6′ > HO-2,2′ > HO-3,3′ > HO-4,4′. Under the appropriate conditions of pivaloylation, heptapivalates with either HO-4 or HO-3 free, hexapivalates with either HO-4,4′ or HO-3′,4 free, and pentapivalates with HO-3′,4,4′ free were obtained. In addition, selective pivaloyation of trehalose 2,2′,3,3′-tetrapivalate afforded the 4,4′-diol and the non-symmetrical 4,4′,6′-triol. The 4-ol, the major heptapivalate, was a convenient starting material for the syntheses of 4-azido-4-deoxy- and 4-amino-4-deoxy-trehalose, together with their 4-epimers, and 4-chloro-4-deoxy-α-D-galactopyranosyl α-D-glucopyranoside. The 4,4′,6′-triol was utilised as a synthetic precursor of 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 4-chloro-4-deoxy-α-D-galactopyranoside and its triazido and triamino analogues.

INTRODUCTION

Derivatisation of the non-reducing disaccharide trehalose at selected positions depends upon the use of appropriate protecting groups[1]. A detailed study of the reaction of sucrose with pivaloyl chloride revealed that this hindered acid chloride showed a high degree of specificity and flexibility leading to the formation of a range of di-, tri-, tetra-, penta-, hexa-, and hepta-pivalates of unique value in synthesis[2]. We now report the application of this reagent to trehalose.

RESULTS AND DISCUSSION

A suspension of anhydrous trehalose in dry pyridine was reacted with 12 equiv. of pivaloyl chloride, initially at $-20°$ and then at room temperature. After 72 h, three major products had been formed (t.l.c.) which were readily isolated by column chromatography. The most mobile component was the octapivalate, which was isolated crystalline (16%). Eluted next were the heptapivalates **4** (9.5%) and **3** (61%), the latter being crystalline. The structures of **3** and **4** were elucidated from their respective ^{1}H-n.m.r. spectra. The spectrum of **3** contained only seven resonances to low field of δ 5 and, by comparison with the spectrum of the octapivalate, it was clear that one of the

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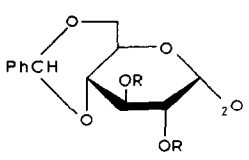
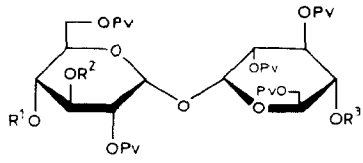


1 R = H
2 R = Pv



3 R^1 = H, R^2 = R^3 = Pv
4 R^1 = R^3 = Pv, R^2 = H
5 R^1 = Pv, R^2 = R^3 = H
6 R^1 = R^3 = H, R^2 = Pv
7 R^1 = R^2 = R^3 = H
8 R^1 = R^3 = Ms, R^2 = Pv
9 R^1 = Pv, R^2 = R^3 = Ms
10 R^1 = Ms, R^2 = R^3 = Pv

H-4 resonances had moved upfield to δ 3.52, thus revealing a hydroxyl group at one of the 4-positions. Similarly, for **4**, one of the H-3 resonances was absent from the region to low field of δ 5, and was located in the upfield region overlapped with the resonances for H-5,5′ and H-6,6′, thus showing that it was the 3-ol.

Repetition of the above reaction with 7 equiv. of pivaloyl chloride yielded a mixture of three new products, which was readily fractionated by column chromatography to give the hexapivalates **5** (38%) and **6** (31%) together with a pentapivalate **7** (19%). The ^{1}H-n.m.r. spectrum of **6** indicated symmetrical substitution and the high-field position (δ 3.36) of the H-4,4′ resonance was consistent with a 4,4′-diol. The spectrum of **5** indicated a non-symmetrical structure and, since one each of the H-3 and H-4 resonances was absent from the downfield part of the spectrum, **5** was either the 3,4- or the 3,4′-diol. The mass spectrum of **5** contained an intense fragment ion at *m/z* 415 ($GlcPv_3^+$) resulting from the cleavage at the glycosidic linkage, which indicated that each glucosyl unit was trisubstituted; hence, **5** has a 3,4′-diol structure.

The ^{1}H-n.m.r. spectrum of the pentapivalate **7** contained five resonances to low field of δ 4.8, and the resonances due to H-3′,4,4′ were located at higher field (δ 3.39–4.04). Hence, **7** was the 3′,4,4′-triol.

Reaction of 2,3,2′,3′-tetra-*O*-pivaloyl-α,α-trehalose (**11**), obtained from 4,6:4′,6′-di-*O*-benzylidene-α,α-trehalose[3] (**1**) by pivaloylation followed by acid hydrolysis, with 1.35 equiv. of pivaloyl chloride followed by column chromatography gave the 4,4′-diol **6** (38%) and the 4,4′,6-triol **12** (48%), the structure of which was readily assigned from its ^{1}H-n.m.r. spectrum.

In general, these results illustrate that pivaloylation of trehalose follows the sequence HO-6,6′, HO-2,2′, HO-3,3′ and finally at the more hindered HO-4,4′. This reactivity profile is identical to that observed for the benzoylation of methyl α-D-glucopyranoside[3], but is significantly different from the results obtained on the selective pivaloyation of sucrose[2] in which the HO-2 had an abnormally low reactivity, compared to that in methyl α-D-glucopyranoside.

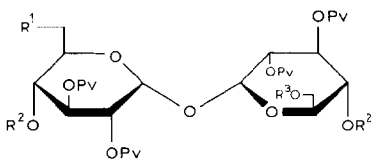
The ready availability of the above partially pivaloylated trehaloses permitted the

synthesis of some non-symmetrically substituted chlorodeoxy- and aminodeoxy-trehaloses. Interest in these derivatives stems from their biological activity. For example, certain aminodeoxytrehaloses show antimicrobial activity[4], and an extremely bitter taste results when certain hydroxyl groups in trehalose are replaced by chloro groups[5], which is in marked contrast to the enhanced sweet taste of many chloro-sucroses[6]. Thus, 4,6-dichloro-4,6-dideoxy-*α*-D-galactopyranosyl 1,6-dichloro-1,6-dideoxy-*β*-D-fructofuranoside is 600 times sweeter than sucrose[6], whereas the isomeric 4,6-dichloro-4,6-dideoxy-*α*-D-galactopyranosyl 4,6-dichloro-4,6-dideoxy-*α*-D-galactopyranoside has an intensely bitter taste[5]. Some related chlorinated trehalose derivatives have been synthesised for assessment of their organoleptic properties.

Treatment of the 4-ol **3** with sulphuryl chloride gave the 4-chloro derivative **15** with inversion of configuration at C-4, which on depivaloylation afforded 4-chloro-4-deoxy-*α*-D-galactopyranosyl *α*-D-glucopyranoside (**16**) as a syrup.

Reaction of **15** with sodium azide in hexamethylphosphoric triamide followed by chromatography gave, first, the 4-ene **29** (39%) and then the crystalline 4-azido-*gluco* isomer **24** (48%). *O*-Deacylation of **24** gave the crystalline azidodeoxytrehalose **25**, which was characterised as the hepta-acetate **26**. Catalytic hydrogenation of **25** afforded 4-amino-4-deoxytrehalose (**27**) as a syrup. This compound has been isolated crystalline from the fermentation of a *Streptomyces* species[7]. Our sample failed to crystallise, even as the hydrochloride, but its $[\alpha]_D$value agreed with that of the natural product and it afforded a crystalline octa-acetyl derivative **28**, which has not been described previously.

The syrupy 4-mesylate **10**, derived from the 4-ol **3**, readily reacted with sodium



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12 $R^1 = OPv, R^2 = R^3 = H$
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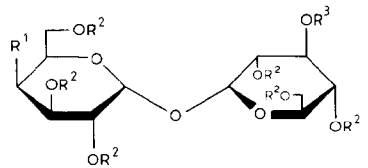
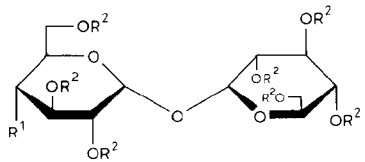
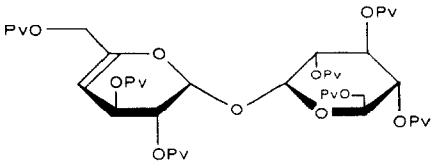
14 $R^1 = Cl, R^2 = R^3 = Ms$



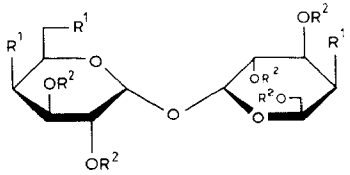
15 $R^1 = Cl, R^2 = R^3 = Pv$
16 $R^1 = Cl, R^2 = R^3 = H$
17 $R^1 = Cl, R^2 = Pv, R^3 = Ms$
18 $R^1 = N_3, R^2 = Pv, R^3 = Ms$
19 $R^1 = N_3, R^2 = R^3 = Pv$
20 $R^1 = N_3, R^2 = R^3 = H$
21 $R^1 = N_3, R^2 = R^3 = Ac$
22 $R^1 = NH_2, R^2 = R^3 = H$
23 $R^1 = NHAc, R^2 = R^3 = Ac$



24 $R^1 = N_3, R^2 = Pv$
25 $R^1 = N_3, R^2 = H$
26 $R^1 = N_3, R^2 = Ac$
27 $R^1 = NH_2, R^2 = H$
28 $R^1 = NHAc, R^2 = Ac$



29



30 R^1 = Cl, R^2 = Pv
31 R^1 = Cl, R^2 = H
32 R^1 = N_3, R^2 = Pv
33 R^1 = N_3, R^2 = H
34 R^1 = N_3, R^2 = Ac
35 R^1 = NH_2, R^2 = H
36 R^1 = NAc, R^2 = Ac

azide in hexamethylphosphoric triamide to give the crystalline *galacto*-4-azide **19** (77%), which was *O*-deacylated and then catalytically reduced to the syrupy amine **22**, characterised as its crystalline octa-acetyl derivative **23**.

When the 3,4′-dimesylate **9**, derived from **5**, was treated with either sodium azide or lithium chloride under similar conditions, it afforded the 4-azide **18** and the 4-chloride **17**, respectively, by selective substitution of the MsO-4′; no displacement occurred at C-3 due to unfavourable steric constraints in the transition states[8].

The 4,4′,6′-trimesylate **13**, prepared (81%) from the 4,4′,6′-triol **11**, was accompanied by a side product (**14**, 11%) resulting from partial displacement of the MsO-6′ by chloride anion. Similar side-products are often encountered during sulphonylations at primary positions[9]. Reaction of **13** with azide anion in hexamethylphosphoric triamide afforded the triazide **32** with inversion at C-4 and C-4′. The crystalline *galacto*-trehalose derivative **33** was isolated on de-esterification of **32** and further characterised as its penta-acetate **34**. Catalytic reduction of **33** then afforded a syrupy triamine **35**, which was characterised as its crystalline octa-acetyl derivative **36**. In an analogous manner, the 4,4′,6-triol **11** was also converted into 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 4-chloro-4-deoxy-α-D-galactopyranoside (**31**).

EXPERIMENTAL

General. — Unless otherwise stated, optical rotations are for ~1% solutions in chloroform at 18–22°. Column chromatography was performed on Silica Gel G (Merck, 7734). Acetylations and mesylations were conducted by dissolving the compound in dry pyridine (10 mL.g^{-1}) and adding either acetic anhydride (10 mL.g^{-1}) or an excess of mesyl chloride as appropriate. The reactions were then processed by the addition of ice–water, followed by either collection of the product if crystalline or, if not, extraction into chloroform. For the n.m.r. data, where given, the primed numbers apply to the ring containing the least number of pivaloyl groups; where this does not differentiate the two rings, then the glucopyranosyl ring is the non-primed ring. For the few compounds in which this cannot differentiate the two rings, then the ring with the pivaloyl groups situated at the lowest numerical positions is given non-primed numbers.

Selective pivaloylation of α,α-trehalose with pivaloyl chloride. — (*a*) *With 12 equiv.* To a suspension of anhydrous trehalose (12.5 g, 36.5 mmol) in dry pyridine (150 mL) at −20° was added pivaloyl chloride (54 mL, 438.4 mmol) dropwise. The mixture was stirred at −20° for a further 30 min and then at room temperature for 3 days, when t.l.c. (ether–light petroleum, 2:1) revealed three products, the least mobile being the major. The mixture was poured into cold water, the products were extracted with chloroform, and the extract was concentrated. Column chromatography (light petroleum–ether, 7:2) of the residue gave, first, trehalose octapivalate (5.75 g, 16%), m.p. 169–171° (from ether–light petroleum), $[\alpha]_D$ +111° (Found: C, 61.4; H, 8.8. $C_{52}H_{86}O_{19}$ calc.: C, 61.5; H, 8.5%). ^{1}H-N.m.r. data (220 MHz, $CDCl_3$): δ 5.43 (d, 2 H, $J_{1,2}$ 4.0 Hz, H-1,1′), 5.00 (dd, 2 H, $J_{2,3}$ 10.0 Hz, H-2,2′), 5.59 (t, 2 H, $J_{3,4}$ 9.5 Hz, H-3,3′), 5.13 (t, 2 H, $J_{4,5}$ 10.0 Hz, H-4,4′), 3.82 (m, 2 H, H-5,5′), 4.13 (dd, 2 H, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 12.5 Hz, H-6a,6′a), 4.00 (dd, 2 H, $J_{5,6b}$ 5.0, H-6b,6′b), 1.0–1.3 (72 H, 8 CMe_3).

Eluted second was 2,4,6-tri-*O*-pivaloyl-α-D-glucopyranosyl 2,3,4,6-tetra-*O*-pivaloyl-α-D-glucopyranoside (**4**; 3.23 g, 9.5%), $[\alpha]_D$ +109° (Found: C, 60.5; H, 8.2. $C_{47}H_{78}O_{18}$ calc.: C, 60.65; H, 8.4%). ^{1}H-N.m.r. data (90 MHz, $CDCl_3$): δ 5.32 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or H-1′), 5.38 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1′ or H-1), 4.91 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2′), 5.02 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′ or H-2), 5.63 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 4.95 (t, 2 H, $J_{4,5}$ 10.0 Hz, H-4 or H-4′), 5.13 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4′ or H-4), 4.0–4.2 (m, 7 H, H-3′,5,5′,6a,6b,6′a,6′b), 1.1–1.3 (63 H, 7 CMe_3).

Eluted last was the 2,2′,3,3′,4,6,6′-heptapivalate **3** (20.7 g, 61%), m.p. 174–176° (from dichloromethane–ethanol), $[\alpha]_D$ +120° (Found: C, 60.45; H, 8.3. $C_{47}H_{78}O_{18}$ calc.: C, 60.65; H, 8.4%). ^{1}H-N.m.r. data (220 MHz, $CDCl_3$): δ 5.43 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or H-1′), 5.35 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1′ or H-1), 5.02 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2′), 5.00 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′ or H-2), 5.60 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.31 (t, 1 H, $J_{3',4'}$ 9.5 Hz, H-3′), 5.13 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.52 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4′), 3.87 (m, 1 H, H-5), 3.70 (m, 1 H, H-5′), 3.90–4.43 (cm, 4 H, H-6,6,6′,6′), 1.1–1.3 (63 H, 7 CMe_3).

Mesylation of **3** afforded the syrupy 4-mesylate **10** (89%), $[\alpha]_D$ +115° (Found: C, 57.15; H, 7.8; S, 3.25. $C_{48}H_{80}O_{20}S$ calc.: C, 57.15; H, 7.95; S, 3.2%). ^{1}H-N.m.r. data (90 MHz, C_6D_6): δ 5.56 (d, 2 H, $J_{1,2}$ 4.0 Hz, H-1,1′), 4.97 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2′), 4.91 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′ or H-2), 5.80 (t, 2 H, $J_{3,4}$ 9.5 Hz, H-3,3′), 5.37 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.63 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4′), 4.5–4.0 (m, 6 H, H-5,5′,6,6,6′,6′), 2.47 (s, 3 H, SMe), 1.1–1.3 (54 H, 6 CMe_3).

(*b*) *With 7 equiv.* The above reaction was repeated with 7 equiv. of pivaloyl chloride (31.45 mL, 0.255 mol). T.l.c. (ether–light petroleum, 3:1) revealed three major products. Column chromatography using ether–light petroleum (2:1) gave, first, 2,3,6-tri-*O*-pivaloyl-α-D-glucopyranosyl 2,4,6-tri-*O*-pivaloyl-α-D-glucopyranoside (**5**; 11.6 g, 38%), $[\alpha]_D$ +116° (Found: C, 59.85; H, 8.4. $C_{42}H_{70}O_{17}$ calc.: C, 59.6; H, 8.3%). ^{1}H-N.m.r. data (220 MHz, $CDCl_3$): δ 5.34 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or H-1′), 5.31 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1′ or H-1), 4.98 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2′), 4.89 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′ or H-2), 5.38 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 4.96 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4′), 3.48 (m, 1 H, H-4), 3.75–4.0 (m, 2 H, H-5,5′), 4.1–4.3 (m, 5 H, H-3′,6,6,6′,6′), 1.1–1.3 (54 H, 6 CMe_3).

Mesylation of **5** afforded the syrupy dimesylate **9** (89% after chromatography), $[\alpha]_D$ +120° (Found: C, 53.0; H, 7.5; S, 6.2. $C_{44}H_{74}O_{21}S_2$ calc.: C, 52.7; H, 7.4; S, 6.4%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): 5.70 (d, 1 H, $J_{1,2}$ 4 Hz, H-1 or H-1'); 5.64 (d, 1 H, $J_{1,2}$ 4 Hz, H-1' or H-1), 5.07 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2 or H-2'), 5.02 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2 or H-2'), 5.94 (t, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.49 (t, 1 H, $J_{3',4'}$ 10 Hz, H-3'), 4.79 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.37 (t, 1 H, $J_{4',5'}$ 10 Hz, H-4'), 4.25 (m, 2 H, H-5,5'), 4.85 (dd, 1 H, $J_{5,6}$ 2 Hz, $J_{6a,6b}$ 12 Hz, H-6a or H-6'a), 4.65 (d, 1 H, $J_{5,6}$ 0 Hz, H-6a or H-6b), 4.44 (dd, 1 H, $J_{5,6b}$ 6 Hz, H-6b or H-6'b), 4.38 (dd, 1 H, $J_{5,6b}$ 6 Hz, H-6b or H-6'b), 2.90 (s, 6H, MeS), 1.2–1.3 (54 H, 6 CMe_3).

Further elution gave the symmetrical 2,3,6,2',3',6'-hexapivalate **6** (9.43 g, 31%), $[\alpha]_D$ +115° (Found: C, 59.3; H, 8.2. $C_{42}H_{70}O_{17}$ calc.: C, 59.6; H, 8.3%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): δ 5.65 (d, 2 H, $J_{1,2}$ 4.0 Hz, H-1,1'), 5.08 (dd, 2 H, $J_{2,3}$ 10.0 Hz, H-2,2'), 5.66 (t, 2 H, $J_{3,4}$ 9.5 Hz, H-3,3'), 3.36 (t, 2 H, $J_{4,5}$ 10.0 Hz, H-4,4'), 4.01 (t, 2 H, H-5,5'), 4.52 (dd, 2 H, $J_{5,6a}$ 1, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.26 (dd, 1 H, $J_{5,6b}$ 7.0 Hz, H-6b), 1.1–1.3 (54 H, 6 CMe_3).

Mesylation of **6** afforded the 4,4'-dimesylate **8** (92%), m.p. 113° (from ether), $[\alpha]_D$ +123° (Found: C, 52.45; H, 7.25; S, 6.6. $C_{44}H_{74}O_{21}S_2$ calc.: C, 52.7; H, 7.4; S, 6.4%). ^{1}H-N.m.r. data (100 MHz, $CDCl_3$): δ 5.34 (d, 2 H, $J_{1,2}$ 4.0 Hz, H-1,1'), 4.88 (dd, 2 H, $J_{2,3}$ 10.0 Hz, H-2,2'), 5.53 (t, 2 H, $J_{3,4}$ 9.5 Hz, H-3,3'), 4.72 (t, 2 H, $J_{4,5}$ 10.0 Hz, H-4,4'), 3.76 (dd, 2 H, H-5,5'), 4.37 (dd, 2 H, $J_{5,6a}$ 1, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.07 (dd, 1 H, $J_{5,6b}$ 5.0 Hz, H-6b), 2.93 (s, 6 H, MeS), 1.2–1.3 (54 H, 6 CMe_3).

Eluted last was 2,6-di-*O*-pivaloyl-α-D-glucopyranosyl 2,3,6-tri-*O*-pivaloyl-α-D-glucopyranoside (**7**; 5.3 g, 19%), $[\alpha]_D$ +107° (Found: C, 58.0; H, 8.15. $C_{37}H_{62}O_{16}$ calc.: C, 58.25; H, 8.15%). ^{1}H-N.m.r. data (220 MHz, $CDCl_3$): δ 5.34 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or H-1'), 5.31 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1' or H-1), 4.95 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2'), 4.78 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2' or H-2), 5.38 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 4.04 (t, 1 H, $J_{3',4'}$ 9.5 Hz, H-3'), 3.49 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4 or H-4'), 3.39 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4 or H-4'), 3.86 (m, 1 H, H-5 or H-5'), 3.43 (m, 1 H, H-5 or H-5'), 4.1–4.3 (m, 4 H, H-6,6,6',6'), 1.1–1.3 (45 H, 5 CMe_3).

4,6-O-Benzylidine-2,3-di-O-pivaloyl-α-D-glucopyranosyl 4,6-O-benzylidine-2,3-di-O-pivaloyl-α-D-glucopyranoside (**2**). — To a solution of 4,6:4',6'-di-*O*-benzylidene-α,α-trehalose[3] (**1**; 10 g, 19.3 mmol) in anhydrous pyridine (150 mL) was added pivaloyl chloride (14 mL, 114 mmol) dropwise at room temperature and the mixture was kept for 5 days at room temperature; t.l.c. (ether–light petroleum, 3:1) then indicated that the reaction was complete. The mixture was poured into ice–water, and the precipitate was collected, dried, and recrystallised from dichloromethane–ethanol to give **2** (15 g, 91%), m.p. 260–261°, $[\alpha]_D$ +76° (Found: C, 64.6; H, 7.4. $C_{46}H_{62}O_{15}$ calc.: C, 64.65; H, 7.25%).

2,3-Di-O-pivaloyl-α-D-glucopyranosyl 2,3-di-O-pivaloyl-α-D-glucopyranoside (**11**). — To a solution of **2** (10 g) in dichloromethane (100 mL) was added methanolic 1% hydrogen chloride (40 mL), and the mixture was kept at room temperature for 18 h; t.l.c. (dichloromethane–ethyl acetate, 4:1) then indicated that the reaction was complete and revealed one slower-moving product. The solution was neutralised with lead carbonate and concentrated to dryness, and the residue was recrystallised from ethanol to give **11**

(8 g, 80%), m.p. 248–250°, $[\alpha]_D$ +154° (*c* 1, *N*,*N*-dimethylformamide) (Found: C, 56.5; H, 8.1. $C_{32}H_{54}O_{15}$ calc.: C, 56.6; H, 8.0%).

2,3-Di-O-pivaloyl-α-D-glucopyranosyl 2,3,6-tri-O-pivaloyl-α-D-glucopyranoside (**12**). — Pivaloyl chloride (7.6 mL, 62 mmol) was added dropwise to a stirred solution of **11** (31 g, 45.7 mmol) in anhydrous pyridine at −20°. The mixture was maintained for 45 min at −20°, then at room temperature for 30 h. T.l.c. (ether–light petroleum, 4:1) revealed two major products. The mixture was processed as above and column chromatography (ether–light petroleum, 4:1) of the product gave, in the early fractions, the 4,4′-diol **6** (14.5 g, 38%).

Further elution afforded **12** as a syrup (16.6 g, 48%), $[\alpha]_D$ +127° (Found: C, 57.95; H, 8.0. $C_{37}H_{62}O_{16}$ calc.: C, 58.3; H, 8.15%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): δ 5.65 (cm, 4 H, H-1,1′,3,3′), 5.00 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 10.0 Hz, H-2 or H-2′), 4.90 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 10.0 Hz, H-2′ or H-2), 3.4–4.5 (cm, 8 H, H-4,4′,5,5′,6,6,6′,6′), 1.1–1.3 (63 H, 7 CMe_3).

4,6-Di-O-mesyl-2,3-di-O-pivaloyl-α-D-glucopyranosyl 4-O-mesyl-2,3,6-tri-O-pivaloyl-α-D-glucopyranoside (**13**). — Mesyl chloride (6 mL, 77.6 mmol) was added dropwise to an ice-cold solution of **12** (9.6 g, 12.6 mmol) in dry pyridine (100 mL). The mixture was kept at room temperature for 20 h, when t.l.c. (ether–light petroleum, 3:1) revealed two products. The mixture was then processed in the usual way, and column chromatography (ether–light petroleum, 1:2) of the product gave 6-chloro-6-deoxy-4-*O*-mesyl-2,3-di-*O*-pivaloyl-α-D-glucopyranosyl 4-*O*-mesyl-2,3,6-tri-*O*-pivaloyl-α-D-glucopyranoside (**14**, 1.3 g, 11%), m.p. 120° (from dichloromethane–ethanol), $[\alpha]_D$ +117° (Found: C, 49.75; H, 6.8; Cl, 3.7; S, 6.8. $C_{39}H_{63}ClO_{19}S_2$ calc.: C, 50.0; H, 6.95; Cl, 3.8; S, 6.8%). ^{1}H-N.m.r. data (90 MHz, C_6D_6): δ 5.58 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or H-1′), 5.50 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1′ or H-1), 4.99 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2′), 4.90 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′ or H-2), 5.74 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3 or H-3′), 5.82 (t, 1 H, $J_{3',4'}$ 9.5 Hz, H-3′ or H-3), 4.68 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4 or H-4′), 4.66 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4′ or H-4), 3.7–4.2 (m, 6 H, H-5,5′,6,6,6′,6′), 2.50, 2.41 (2 s, 6 H, SMe), 1.1–1.3 (45 H, 5 CMe_3).

Later fractions contained syrupy **13** (10.1 g, 81%), $[\alpha]_D$ +120° (Found: C, 48.45; H, 6.65; S, 9.65. $C_{40}H_{68}O_{22}S_3$ calc.: C, 48.2; H, 6.8; S, 9.65%). ^{1}H-N.m.r. data (90 MHz, C_6D_6): δ 5.56 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or H-1′), 5.50 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1′ or H-1), 4.99 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2′), 4.90 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2′ or H-2), 5.84 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3 or H-3′), 5.82 (t, 1 H, $J_{3',4'}$ 9.5 Hz, H-3′ or H-3), 4.72 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4 or H-4′), 4.68 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4′ or H-4), 3.9–4.2 (m, 6 H, H-5,5′,6,6,6′,6′), 2.55, 2.51, 2.49 (3 s, 9 H, SMe), 1.1–1.3 (45 H, 5 CMe_3).

4-Chloro-4-deoxy-2,3,6-tri-O-pivaloyl-α-D-galactopyranosyl 3-O-mesyl-2,4,6-tri-O-pivaloyl-α-D-glucopyranoside (**17**). — A warm solution of the 3′,4-dimesylate **8** (5 g, 5 mmol) in hexamethylphosphoric triamide (25 mL) containing a small crystal of iodine was heated at 90–95° (bath) with lithium chloride (3.1 g, 73 mmol) for 36 h. T.l.c. (ether–light petroleum, 1:1) then revealed a faster-moving component and several slower-moving minor components. The mixture was poured into stirred ice–water, and the precipitate was collected, washed well with water, and recrystallised from ether–ethanol to give **17** (3.25 g, 69%), m.p. 135–137°, $[\alpha]_D$ +135° (Found: C, 54.5; H, 7.4; Cl, 3.6, S, 3.25. $C_{43}H_{71}ClO_{18}S$ calc.: C, 54.75; H, 7.55; Cl 3.8; S, 3.4%). ^{1}H-N.m.r. data (220

MHz, C_6D_6): δ 5.70 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), δ 5.63 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1'), 5.10 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.56 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2'), 5.42 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.64 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3'), 5.27 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.59 (dd, 1 H, $J_{4',5'}$ 1.5 Hz, H-4'), 3.9–4.4 (m, 6 H, H-5,5',6,6,6',6'), 2.14 (s, 3 H, SMe), 1.1–1.3 (54 H, 6 CMe_3).

*4-Azido-4-deoxy-2,3,6-tri-*O*-pivaloyl-α-*D*-galactopyranosyl 3-*O*-mesyl-2,4,6-tri-*O*-pivaloyl-α-*D*-glucopyranoside* (**18**). — The above reaction was repeated using sodium azide (4.9 g, 75.4 mmol) instead of the chloride. The mixture was then poured into ice–water, and the product was collected and recrystallised from boiling chloroform–ethanol to give the azide **18** (3.65 g, 77%), m.p. 178–180°, $[\alpha]_D$ +117° (Found: C, 54.75; H, 7.7; N, 4.2; S, 3.2. $C_{43}H_{71}N_3O_{18}S$ calc.: C, 54.35; H, 7.5; N, 4.4; S, 3.4%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): δ 5.65 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), δ 5.56 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1'), 5.06 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.49 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2'), 5.39 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.62 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3'), 5.25 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.90 (dd, 1 H, $J_{4',5'}$ 1.5 Hz, H-4'), 3.8–4.4 (m, 6 H, H-5,5',6,6,6',6'), 2.14 (s, 3 H, SMe), 1.1–1.3 (54 H, 6 CMe_3).

*4-Chloro-4-deoxy-2,3,6-tri-*O*-pivaloyl-α-*D*-galactopyranosyl 2,3,4,6-tetra-*O*-pivaloyl-α-*D*-glucopyranoside* (**15**). — A solution of the heptapivalate **3** (9 g, 9.7 mmol) in a mixture of chloroform (100 mL) and pyridine (100 mL) at −20° was treated with sulphuryl chloride (2.5 mL, 31 mmol). The mixture was kept at room temperature for 24 h, then concentrated to dryness. Column chromatography (ether–light petroleum, 1:6) of the residue gave syrupy **15** (7.8 g, 85%), $[\alpha]_D$ +131° (Found: C, 59.2; H, 7.9; Cl, 3.6. $C_{47}H_{77}ClO_{17}$ calc.: C, 59.45; H, 8.1; Cl, 3.75%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): δ 5.70 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.57 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1'), 5.08 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.54 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2'), 5.81 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.61 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3'), 5.12 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.54 (dd, 1 H, $J_{4',5'}$ 1.5 Hz, H-4'), 3.9–4.4 (m, 6 H, H-5,5',6,6,6',6'), 1.1–1.3 (63 H, 7 CMe_3).

*4-Azido-4-deoxy-2,3,6-tri-*O*-pivaloyl-α-*D*-glucopyranosyl 2,3,4,6-tetra-*O*-pivaloyl-α-*D*-glucopyranoside* (**24**). — A solution of **15** (15 g) in hexamethylphosphoric triamide (60 mL) containing sodium azide (7 g) was heated at 95–100° for 48 h, when t.l.c. (ether–light petroleum, 1:2) revealed two major and several minor products. The mixture was then stirred vigorously whilst cold water was added, the precipitate was collected, and column chromatography (ether–light petroleum, 1:7) gave, first, 4-deoxy-2,3-di-*O*-pivaloyl-β-L-*threo*-hex-4-enopyranosyl 2,3,4,6-tetra-*O*-pivaloyl-α-D-glucopyranoside (**29**; 5.63 g, 39%), m.p. 158° (from ether), $[\alpha]_D$ +176° (Found C, 61.4; H, 8.4. $C_{47}H_{76}O_{17}$ calc.: C, 61.85; H, 8.3%). ^{1}H-N.m.r. data (220 MHz, $CDCl_3$): δ 5.50 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), δ 5.40 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1'), 4.90 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.25 (dd, 1 H, $J_{2',3'}$ 8.5 Hz, H-2'), 5.54 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-3), 5.48 (dd, 1 H, $J_{3',4'}$ ~2.5 Hz, H-3'), 5.12 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.95 (d, 1 H, H-4'), 4.45 (m, 2 H, H-6,6 or H-6',6'), 3.98 (m, 1 H, H-5), 4.0–4.2 (m, 2 H, H-6,6 or H-6',6'), 1.1–1.3 (63 H, 7 CMe_3).

Further elution afforded **24** (7.25 g, 48%), m.p. 118–120° (from ether), $[\alpha]_D$ +149° (Found C, 59.25; H, 8.0; N, 4.25. $C_{47}H_{77}N_3O_{17}$ calc.: C, 59.1; H, 8.1; N, 4.4%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): δ 5.72 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or H-1'), 5.67 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1' or H-1), 4.98 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2'), 4.94 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2' or H-2), 5.83 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3 or H-3'), 5.75 (t, 1 H, $J_{3',4'}$ 9.5 Hz, H-3' or H-3), 5.15 (t, 1

H, $J_{4,5}$ 10.0 Hz, H-4), 2.96 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4'), 3.7–4.4 (m, 6 H, H-5,5',6,6,6',6'), 1.1–1.3 (54 H, 6 CMe_3).

4-Azido-4-deoxy-α-D-glucopyranosyl α-D-glucopyranoside (**25**). — A solution of **24** (5 g) in methanol (75 mL) was treated with methanolic M sodium methoxide (25 mL) at room temperature for 1 h, then neutralised with Amberlite IR-120(H^+) resin, and concentrated to give **25** (1.5 g, 78%), m.p. 142–144° (from ethanol), $[\alpha]_D$ +197° (*c* 1, methanol) (Found: C, 39.4; H, 5.8; N, 11.4. $C_{12}H_{21}N_3O_{10}$ calc.: C, 39.25; H, 5.7; N, 11.45%).

Acetylation of **25** afforded the hepta-acetate **26** (87%), m.p. 126–128° (from ether), $[\alpha]_D$ +144° (Found: C, 47.35; H, 5.25; N, 6.25. $C_{26}H_{35}N_3O_{17}$ calc.: C, 47.2; H, 5.3; N, 6.35%). ^{1}H-N.m.r. data (90 MHz, C_6D_6): δ 5.32 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or H-1'), 5.28 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1' or H-1), 5.09 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2 or H-2'), 4.98 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2' or H-2), 5.74 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3 or H-3'), 5.72 (t, 1 H, $J_{3',4'}$ 9.5 Hz, H-3' or H-3), 5.15 (t, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.16 (t, 1 H, $J_{4',5'}$ 10.0 Hz, H-4'), 3.8–4.3 (m, 6 H, H-5,5',6,6,6',6'), 1.7–1.9 (21 H, 7 Ac).

4-Amino-4-deoxy-α-D-glucopyranosyl α-D-glucopyranoside (**27**). — A solution of **25** (0.7 g) in methanol (50 mL) was hydrogenated over 10% Pd–C (150 mg) at 50 p.s.i. for 24 h at room temperature, then filtered through Hyflo Supercel, and concentrated to give a hygroscopic syrup, $[\alpha]_D$ + 175° (c 1, water), which failed to crystallise, and for which a satisfactory elemental analysis could not be obtained; lit.[7] (for the monohydrate), m.p. 140°, $[\alpha]_D$ +179° (water).

Acetylation of **27** afforded the octa-acetyl derivative **28** (87%), m.p. 134–135° (from ether–ethanol), $[\alpha]_D$ +129° (Found: C, 49.5; H, 5.85; N, 2.1. $C_{28}H_{39}NO_{18}$ calc.: C, 49.65; H, 5.75; N, 2.05%).

4-Azido-4-deoxy-2,3,6-tri-O-pivaloyl-α-D-galactopyranosyl 2,3,4,6-tetra-O-pivaloyl-α-D-glucopyranoside (**19**). — A solution of the 4-mesylate **10** (6.75 g) in hexamethylphosphoric triamide (30 mL) was heated with sodium azide (2.2 g) for 36 h at 90° (bath), when t.l.c. (ether–light petroleum, 1:2) revealed a single product. Water was added to the mixture, and the product was collected and recrystallised from ethanol to give **19**, m.p. 74–76°, $[\alpha]_D$ +113° (Found: C, 59.0; H, 8.2; N, 4.3. $C_{47}H_{77}N_3O_{17}$ calc.: C, 59.1; H, 8.1; N, 4.4%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): δ 5.69 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.53 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1'), 5.07 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.53 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-2'), 5.82 (t, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.65 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, H-3'), 5.10 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.87 (dd, 1 H, $J_{4',5'}$ 1.5 Hz, H-4'), 3.9–4.4 (m, 6 H, H-5,5',6,6,6',6'), 1.1–1.3 (54 H, 6 CMe_3).

4-Azido-4-deoxy-α-D-galactopyranosyl α-D-glucopyranoside (**20**). — The azide **19** (5 g) was *O*-depivaloylated, as described above for **24**, to give **20** (1.6 g, 83%), m.p. 109–111°, $[\alpha]_D$ +154° (*c* 1, methanol) (Found: C, 39.4; H, 5.6; N, 11.4. $C_{12}H_{21}N_3O_{10}$ calc.: C, 39.25; H, 5.7; N, 11.45%).

Acetylation of **20** afforded the hepta-acetate **21** (81%), m.p. 59–61° (from acetone), $[\alpha]_D$ +145° (Found C, 47.1; H, 5.15; N, 6.2. $C_{26}H_{35}N_3O_{17}$ calc.: C, 47.2; H, 5.3; N, 6.35%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): δ 5.42 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.33 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1'), 5.17 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2), 5.58 (m, 2 H, H-2',3'), 5.80 (t, 1 H, $J_{3,4}$

9.5 Hz, H-3), 5.19 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.93 (bs, 1 H, $J_{4',5'}$ 1.5 Hz, H-4'), 4.05–4.3 (m, 6 H, H-5,5',6,6,6',6'), 1.7–1.85 (7 s, 21 H, 7 Ac).

*4-Amino-4-deoxy-α-*D*-galactopyranosyl α-*D*-glucopyranoside* (**22**). — Hydrogenation of the 4-azide **20** (1 g) was achieved in methanol (50 mL) with 10% Pd–C at 50 p.s.i. for 24 h at room temperature. The mixture was filtered and concentrated to dryness to give syrupy **22** (0.75 g, 81%), $[\alpha]_D$ +169° (*c* 1, methanol) (Found: C, 42.1; H, 6.9; N, 4.0. $C_{12}H_{23}NO_{10}$ calc.: C, 42.25; H, 6.75; N, 4.1%).

Acetylation of **22** afforded the octa-acetate **23** (74%), m.p. 134–136° (from ether), $[\alpha]_D$ +131° (Found: C, 49.45; H, 5.65; N, 2.2. $C_{28}H_{39}NO_{18}$ calc.: C, 49.65; H, 5.75; N, 2.1%).

*4,6-Dichloro-4,6-dideoxy-2,3-di-*O*-pivaloyl-α-*D*-galactopyranosyl 4-chloro-4-deoxy-2,3,6-tri-*O*-pivaloyl-α-*D*-galactopyranoside* (**30**). — To a solution of the triol **12** (5.8 g. 7.6 mmol) in chloroform (75 mL) and dry pyridine (75 mL) at −20° was added sulphuryl chloride (3.8 mL, 47 mmol). The mixture was maintained for 30 min at −25°, then for 24 h at room temperature, and concentrated to dryness. Column chromatography (ether–light petroleum, 1:7) of the residue gave syrupy **30**, $[\alpha]_D$ +176° (Found: C, 54.7; H, 7.5; Cl, 13.2. $C_{37}H_{59}Cl_3O_{13}$ calc.: C, 54.3; H, 7.2; Cl, 13.0%). ^{1}H-N.m.r. data (220 MHz, C_6D_6): δ 5.60 [m, 5 H, H-1,1',2(or 2'),3,3'], 5.54 (dd, 1 H, $J_{1,2}$ 4.0, $J_{2,3}$ 10.0 Hz, H-2 or H-2'), 4.77 (bd, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 1 Hz, H-4 or H-4'), 4.54 (bd, 1 H, $J_{3,4}$ ~3, $J_{4,5}$ ~1 Hz, H-4 or H-4'), 4.1–4.3 (cm, 4 H, H-5,5',6,6), 3.65 (cm, 2 H, H-6',6'), 1.2–1.3 (45 H, 5 CMe_3)

O-Depivaloylation of **30** in the usual way afforded syrupy 4,6-dichloro-4,6-dideoxy-α-D-galactopyranosyl 4-chloro-4-deoxy-α-D-galactopyranoside (**31**, 69%) after column chromatography (chloroform–methanol, 6:1), $[\alpha]_D$ +229° (*c* 1, methanol) (Found C, 36.0; H, 4.6; Cl, 26.6. $C_{12}H_{19}Cl_3O_8$ calc.: C, 36.2; H, 4.8; Cl, 26.8%).

*4,6-Diazido-4,6-dideoxy-2,3-di-*O*-pivaloyl-α-*D*-galactopyranosyl 4-azido-4-deoxy-2,3,6-tri-*O*-pivaloyl-α-*D*-galactopyranoside* (**32**). — A solution of the trimesylate **13** (9 g) in hexamethylphosphoric triamide (40 mL) was heated at 90° (bath) with sodium azide (6 g) for 42 h, when t.l.c. (ether–light petroleum, 2:5) indicated complete reaction. Water was added to the mixture with vigorous stirring, and the precipitate was collected and recrystallised from boiling dichloromethane–ethanol to give **32** (6.3 g, 83%), m.p. 145°, $[\alpha]_D$ +134° (Found: C, 52.85; H, 6.9; N, 14.9. $C_{37}H_{59}N_9O_{13}$ calc.: C, 53.05; H, 7.05; N, 15.05%).

O-Depivaloylation of **32** in the usual way afforded 4,6-diazido-4,6-dideoxy-α-D-galactopyranosyl 4-azido-4-deoxy-α-D-galactopyranoside (**33**, 84%), m.p. 110° (from acetone), $[\alpha]_D$ +135° (c 1, methanol) (Found C, 34.9; H, 4.7; N, 30.0. $C_{12}H_{19}N_9O_8$ calc.: C, 34.55; H, 4.55; N, 30.2%).

Acetylation of **33** afforded the penta-acetate **34** (89%), m.p. 133° (from ether), $[\alpha]_D$ +157° (Found: C, 42.4; H, 4.8; N, 19.9. $C_{22}H_{29}N_9O_{13}$ calc.: C, 42.1; H, 4.6; N, 20.1%).

*4,6-Diamino-4,6-dideoxy-α-*D*-galactopyranosyl 4-amino-4-deoxy-α-*D*-galactopyranoside* (**35**). — A solution of **33** (1 g) in methanol was hydrogenated at 50 p.s.i. over 10% Pd–C (0.3 g) for 24 h, then filtered, and concentrated to dryness to give syrupy **35** (0.7 g, 86%). $[\alpha]_D$ +219° (*c* 1, methanol) (Found: C, 42.3; H, 7.5; N, 12.2. $C_{12}H_{25}N_3O_8$ calc.: C, 42.5; H, 7.4; N, 12.4%).

Acetylation of **35** afforded the octa-acetyl derivative **36**, m.p. 295° (from ether), $[\alpha]_D + 196°$ (*c* 1, methyl sulphoxide) (Found: C, 49.6; H, 6.0; N, 6.1. $C_{28}H_{41}N_3O_{16}$ calc.: C, 49.8; H, 6.1; N, 6.2%).

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