Chemical Modification of Trehalose. Part XIV.[1] Some Tetra- and Hexadeoxy-derivatives and their Amino-analogues

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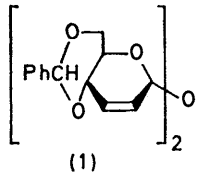
2,2',3,3'-Tetradeoxy-αα-trehalose has been synthesised by palladium-catalysed hydrogenolysis of the 2,2'-diene, 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, which reduced the double bonds and removed the benzylidene substituents simultaneously. The derived tetramesylate underwent replacement of all four sulphonate groups when treated with either azide or benzoate ions to give the *threo*-analogues. Selective displacement of the primary sulphonyloxy-groups was achieved with iodide ion and the 6,6'-di-iodo-derivative was subjected to reductive dehalogenation. The resulting 2.2'.3,3'.6,6'-hexadeoxy-4.4'-dimesylate underwent a ready displacement with azide anion to give the 4,4'-diazide, but when benzoate ion was employed as nucleophile products arising from both nucleophilic displacement and elimination were obtained.

We have previously described the synthesis of several di- and tetra-deoxy-derivatives of the disaccharide αα-trehalose,[2-4] and have now extended these studies to include some further tetra- and some hexa-deoxy-derivatives which contain the 2,2',3,3'-tetradeoxy-system. A suitable starting material for these studies, 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (1), has been described previously.[4] The diene underwent ready reduction over palladium–charcoal to give a tetradeoxy-derivative in high yield. The ^{1}H n.m.r. and i.r. spectra, however, indicated that the product was not the expected dibenzylidene derivative of 2,2',3,3'-tetradeoxytrehalose but the disaccharide itself (2), formed by simultaneous reduction of the double bonds and hydrogenolysis of the benzylidene groups. A closer study of the course of the reduction revealed that it proceeded *via* a multitude of intermediates and that at no stage did one appear to predominate. This behaviour contrasted with that of methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, which underwent selective reduction of the double bond upon hydrogenation over palladium–charcoal.[5] The catalytic hydrogenolytic removal of benzylidene groups has been described previously [6] but it has never become an established and widely used method, owing to its capricious nature. The structure of the tetradeoxytrehalose (2) was firmly established by the ^{1}H n.m.r. spectrum of the derived tetramesylate (3) in which the H-1, H-4, and H-5, and H-6 resonances were readily assigned and were in complete accord with the structure. The methylene protons gave rise to two very broad signals around τ 8·0 and it was not possible to assign individual resonances (Table).

Reaction of the tetramesylate (3) with sodium azide in hexamethylphosphoric triamide resulted in the isolation of a tetra-azide (6) in 74% yield. The structure of the tetra-azide was indicated by the upfield shift of the H-4, H-4', and H-6, H-6' resonances by 1·2—1·5 p.p.m. in the ^{1}H n.m.r. spectrum of (6) as compared to that of (3) (Table). Furthermore the small value of $J_{4,5}$ (1·5 Hz) is characteristic of a 4-equatorial and a 5-axial proton.[7]



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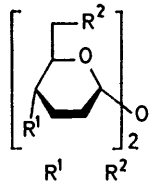
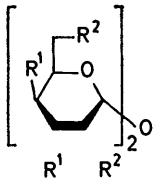
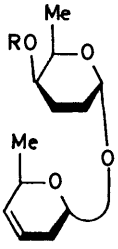


	R^1	R^2
(2)	OH	OH
(3)	OMs	OMs
(4)	OMs	I
(5)	OMs	H



	R^1	R^2
(6)	N_3	N_3
(7)	NH_2	NH_2
(8)	OBz	OBz
(9)	OH	OH
(10)	OMs	OMs
(11)	N_3	H
(12)	NH_2	H
(13)	NHAc	H
(14)	OBz	H
(15)	OH	H
(16)	OMs	H



(17) R = H
(18) R = Ts

The spectrum was similar to that of the related 4,6-diazido-2-*O*-benzoyl-3,4,6-trideoxy-α-D-*lyxo*-hexopyranosyl 4,6-diazido-2-*O*-benzoyl-3,4,6-trideoxy-α-D-*lyxo*-hexopyranoside (except for the H-2 and H-2' resonances).[3] Catalytic hydrogenation of the tetra-azide afforded the syrupy tetra-amine (7) but attempts to

[1] Part XIII, L. Hough, A. K. Palmer, and A. C. Richardson, *J.C.S. Perkin I*, 1973, 784.
[2] L. Hough, A. C. Richardson, and E. Tarelli, *J. Chem. Soc.* (*C*), 1971, 1732.
[3] L. Hough, A. C. Richardson, and E. Tarelli, *J. Chem. Soc.* (*C*), 1971, 2122.
[4] A. C. Richardson and E. Tarelli, *J.C.S. Perkin I*, 1972, 949.
[5] E. L. Albano and D. Horton, *J. Org. Chem.*, 1969, **34**, 3519.
[6] G. R. Barker and J. W. Spoors, *J. Chem. Soc.*, 1956, 1192.
[7] Y. Ali, L. Hough, and A. C. Richardson, *Carbohydrate Res.*, 1970, **14**, 181; M. W. Horner, L. Hough, and A. C. Richardson, *J. Chem. Soc.* (*C*), 1970, 1366; 1971, 99.

characterise it by the formation of a tetra-*N*-acyl derivative failed to give a crystalline derivative.

The tetramesylate (3) also underwent direct replacement of all four sulphonyloxy-groups with benzoate ion to give 2,3-dideoxy-α-D-*threo*-hexopyranosyl 2,3-dideoxy-α-D-*threo*-hexopyranoside tetrabenzoate (8) in 79% yield. De-*O*-benzoylation of (8) gave the parent disaccharide symmetrical derivative, since it contained two CH*Me* doublets at τ 9·0 and 8·8. Furthermore, the spectrum contained three singlets at τ 4·36, 4·80, and 5·50 in the ratio 2 : 2 : 1, the last, broad singlet being assigned to H-4 of a 2,3,6-trideoxy-4-*O*-tosyl-α-D-*threo*-hexopyranosyl system by comparison with the spectrum of the related tetramesylate (10). The middle singlet, also broad,

^{1}H N.m.r. parameters: first-order chemical shifts (τ values) and coupling constants (Hz) at 100 MHz

Compound	(2) [a,b]	(3) [a]	(4) [c]	(5) [a]	(6) [c]	(8) [a]	(10) [a]	(13) [d]	(16) [c]	(18) [c,e] A	(18) [c,e] B
H-1, H-1′	4·50 (d)	4·72 (s)	4·69 (t)	4·96 (t)	4·78 (s)	4·33 (s)	4·56 (s)	5·04 (d)	4·84 (s)	4·80(s)	4·80 (s)
H-2, H-2′	7·6—	7·5—	7·7—	7·75—	7·8—	7·5—	7·8—	7·8—	7·8—	7·8—	7·6 (cm)
H-3, H-3′	8·4 (cm)	8·4 (cm)	8·3 (cm)	8·3 (cm)	8·6 (cm)	8·4 (cm)	8·6 (cm)	8·6 (cm)	8·6 (cm)	8·6 (cm)	4·36 (s)
H-4, H-4′		5·07 (td)	4·56 (cm)	5·70 (cm)	6·36 (s)	4·42 (s)	4·88 (s)	4·9—	5·35 (s)	5·50 (s)	
H-5, H-5′	5·5—	5·87 (dt)		6·24 (dq)	6·08 (td)		5·56 (cm)	5·3 (cm)	6·02 (q)	6·08 (q)	5·79 (qd)
H-6a, H-6a′	6·2 (cm)	5·28 (cm)	6·2—	8·75 (d)	6·53 (dd)	5·2—	5·35 (cm)	9·05 (d)	8·78 (d)	8·80 (d)	9·00 (d)
H-6b, H-6b′			6·85 (cm)		6·82 (dd)	5·5 (cm)					
OMs		6·62	6·92								
		6·71									
$J_{1,2ax}$	*ca.* 2·5	*	*ca.* 2·5	*ca.* 2	*	*	*	*	*	*	*
$J_{1,2eq}$	*ca.* 2·5	*	*ca.* 2·5	*ca.* 2	*	*	*	*	*	*	*
$J_{3ax,4}$		9·7			●	*	*		*	*	
$J_{3eq,4}$		5·5			●	*	*		*	*	
$J_{4,5}$		9·5		9·2	*ca.* 1·5	†	†		*ca.* 1·5	*ca.* 1·5	*ca.* 3
$J_{5,6a}$		*ca.* 3		*ca.* 6	7·5			6·0	6·0	*ca.* 7	*ca.* 7
$J_{5,6b}$		*ca.* 3			5·5						
$J_{6a,6b}$					13						

[a] In [$^2H_5$]pyridine. [b] Hydroxy-resonances at τ 3·64 (d, 4,4′-OH) and 4·08br (s, 6,6′-OH). [c] In [^2H]chloroform. [d] In [$^2H_7$]-*NN*-dimethylformamide. [e] Ring A is the saturated pyranosyl ring.

* Estimated as 2—3 Hz from width of H-1,H-1′ or H-4,H-4′ resonances as appropriate. † Estimated as very small from width of H-4,H-4′ resonance.

(9), which failed to crystallise but was further characterised as its tetramesylate (10). The structures of these derivatives were indicated by the appearance of the H-4,H-4′ resonance as a broadened singlet in the ^{1}H n.m.r. spectra of (8) and (10), showing that the couplings to H-4,H-4′ were all small, in agreement with these protons being equatorial (Table).

Selective displacement of the primary sulphonate groups of (3) with sodium iodide in acetone gave the 6,6′-di-iodo-derivative (4) in 90% yield. Reductive dehalogenation was achieved with the Raney nickel-hydrazine reagent [2] and the hexadeoxy-derivative (5) was isolated in 71% yield, indicative of the convenience of this reagent. The sulphonate groups of (5) were both replaced by azide with inversion of configuration to give the 4,4′-diazide (11), which could not be crystallised but was reduced directly to the syrupy amine (12), isolated as the crystalline di-*N*-acetyl derivative (13) in an overall yield of 82%.

In contrast, the attempted displacement of (5) with sodium benzoate in hexamethylphosphoric triamide resulted in a mixture of at least two products, as indicated by t.l.c., which were more amenable to chromatographic separation after de-*O*-benzoylation of the mixture with sodium methoxide. The mixture was separated by dry column chromatography on silica gel [8] and the two major components, *A* and *B*, were isolated in 55 and 31% yield, respectively. It was subsequently found that *A* was contaminated by residual methyl benzoate (from the debenzoylation step) and that its actual yield lay in the range 44—55%, most probably nearer to the lower limit, since it afforded a crystalline monotosylate ester in 79% yield. The ^{1}H n.m.r. spectrum of the monotosylate indicated that it was a non-

[8] L. Hough, A. K. Palmer, and A. C. Richardson, *J.C.S. Perkin I*, 1972, 2513.

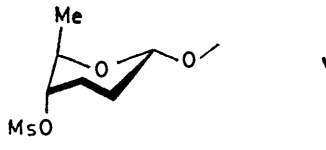
was assigned to the 1-protons and the lowest field singlet was in a position consistent with olefinic protons attached to a six-membered ring. The i.r. spectrum of the product confirmed the presence of unsaturation ($\nu_{max.}$ 1625 cm^{-1}). The double bond must be between C-4 and C-3 because the appearance of both H-6 signals as doublets suggested that both 5-protons were intact. The monotosylate was thus assigned the structure (18). The original product (17) must have arisen from (5) by one of the sulphonyl groups undergoing S_N2 displacement and the other undergoing bimolecular elimination, probably of the *E2C* type.[2,9]

The product *B* was obtained crystalline and converted into the dimesylate (16), the ^{1}H n.m.r. spectrum of which indicated that *B* was the diol (15) and that the dibenzoate (14) was the product of direct substitution of both sulphonyloxy-groups. There was a single high field doublet due to two equivalent CH*Me* groups, only one H-5,H-5′ resonance at τ 6·02, and no resonance which could be considered as being due to olefinic protons. The resonances due to H-4,H-4′ and H-1,H-1′ appeared as broad singlets in similar positions to those observed in the non-symmetrical derivative (18).

The occurrence of elimination in the reaction of (5) is of interest inasmuch as it contrasts with that of (3), which differs only in having 6- and 6′-mesyloxy-groups. In the latter tetrasulphonate ester no elimination was observed although the reaction conditions were essentially the same in both cases. Generally the occurrence of elimination in attempted S_N2 reactions is observed either when the sulphonyloxy-group is axial and flanked by an axial hydrogen atom in the ground state conformation (the correct orientation for an *E2* or *E2C* elimination [2,9]) or when a strongly basic anion is used as the

[9] A. K. Al-Radhi, J. S. Brimacombe, and L. C. N. Tucker, *Carbohydrate Res.*, 1972, **22**, 103.

nucleophile (*e.g.* fluoride [10]). Assuming that the elimination observed in (5) has *E*2 or *E*2*C* characteristics, which is probable since had there been *E*1 character then some elimination of the *cis*-5-protons might have been expected, then the conformation of the transition state of the reaction would approximate to a ground state conformation in which the sulphonyloxy-group is antiperiplanar with the 3-H, that is a $^1C_4$(D), $^{0,3}B$(D), or $B_{1,4}$(D) conformation (or related skew systems), (19)—(21), respectively. The $B_{1,4}$ conformation (21) would be most



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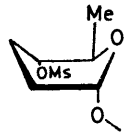

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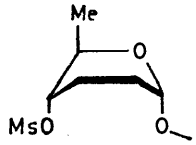

(21)

unlikely because of the diaxial interactions. The most likely explanation as to why (5) gives some elimination product and (3) does not is that the bulk of the 6-substituent prevents the 6-carbon atoms becoming axial and therefore obstructs the conformational change necessary for elimination. Consequently, it seems more probable that the conformation of the transition state is similar to the $^1C_4$(D) conformation (19) in which C-6 must become axial.

A further relevant point is the proportions of the two products (17) and (15) formed in the reaction. We have already discussed the proportions of products formed from trehalose derivatives when two reaction pathways are operative.[2] If x is the molar proportion of the major product formed from one of the hexopyranosyl systems in isolation,* then the yield of the major symmetrical product is given by x^2, that of the minor symmetrical product by $(1 - x)^2$, and that of the non-symmetrical product by $2x(1 - x)$. A value of 0·55 gives calculated values of 30·25% for (15) and 49·5% for (17), close to the observed values of 31 and 50 ± 5%. However, it is difficult to come to firm conclusions regarding an accurate value of x, since the yields were of isolated product rather than of product actually present in the reaction mixture. These considerations suggest that there should have been about 20% of the symmetrical 3,3′-diene present. This compound was neither isolated nor detected and it is possible that, since this compound would be volatile, it might have been lost during the work-up.

The conversion of methyl 2,3,6-trideoxy-4-*O*-mesyl-α-D-*erythro*-hexopyranoside into the *threo*-analogue has been achieved by a related reaction.[11] The authors did not report any products arising from elimination but the low yield (53%) suggested that there may have been another product formed which might have been lost as a result of its high volatility.

* An approximation for this value can be derived from a study of the corresponding methyl α-D-hexopyranoside.

EXPERIMENTAL

Unless otherwise stated, all optical rotations are for chloroform solutions. For other general notes see ref. 2.

2,3-*Dideoxy*-α-D-erythro-*hexopyranosyl* 2,3-*Dideoxy*-α-D-erythro-*hexopyranoside* (2,2′,3,3′-*Tetradeoxytrehalose*).—A suspension of the 2,2′-diene [4] (1) (2 g) in methanol (40 ml) was hydrogenated at 50 lb in^{-2} over palladium–charcoal (0·1 g) for 6 h. The resulting solution was filtered through Hyflo-supercel and evaporated to give a highly crystalline residue. Recrystallisation from propan-2-ol–light petroleum gave the *tetradeoxy-disaccharide* (1·2 g, 97%), m.p. 165—166°, $[\alpha]_D$ +201° (*c* 0·8 in EtOH) (Found: C, 52·0; H, 7·7. $C_{12}H_{22}O_7$ requires C, 51·8; H, 8·0%).

The *tetramesylate* (3) was prepared from (2) in the usual way (94%); m.p. 132—134° (propan-2-ol), $[\alpha]_D$ +124° (*c* 1) (Found: C, 32·9; H, 4·9; S, 21·8. $C_{16}H_{30}O_{15}S_4$ requires C, 32·5; H, 5·1; S, 21·7%).

4,6-*Diazido*-2,3,4,6-*tetradeoxy*-α-D-threo-*hexopyranosyl* 4,6-*Diazido*-2,3,4,6-*tetradeoxy*-α-D-threo-*hexopyranoside* (6).—A mixture of the tetramesylate (3) (1 g) and sodium azide (2 g) in hexamethylphosphoric triamide (5 ml) was maintained at 80° (oil-bath) for 12 h and then poured into water. The white crystalline precipitate was filtered off, washed well with water, and recrystallised from propan-2-ol to give the *tetra-azide* (0·6 g, 74%), m.p. 120—121°, $[\alpha]_D$ +33° (*c* 0·9) (Found: C, 38·3; H, 4·6; N, 44·4. $C_{12}H_{18}O_3N_{12}$ requires C, 38·1; H, 4·8; N, 44·4%).

Hydrogenation of the tetra-azide (0·3 g) in methanol (10 ml) over palladium–charcoal at 50 lb in^{-2} afforded the syrupy tetra-amine (7) (0·19 g, 96%), which failed to crystallise. The i.r. spectrum showed that all azide groups had been reduced ,but the preparation of tetra-*N*-acetyl and tetra-*N*-bemzoyl derivatives failed to give a crystalline product.

4,6-*Di*-O-*benzoyl*-2,3-*dideoxy*-α-D-threo-*hexopyranosyl* 4,6-*Di*-O-*benzoyl*-2,3-*dideoxy*-α-D-threo-*hexopyranoside* (8).—A mixture of the tetramesylate (3) (1·5 g) and sodium benzoate (3 g) in hexamethylphosphoric triamide (15 ml) was kept at 90° (oil-bath) for 48 h, and then poured into water. The resulting white crystalline solid was filtered off, washed well with water, and recrystallised from propan-2-ol to give the *tetrabenzoate* (1·4 g, 79%), m.p. 133—135°, $[\alpha]_D$ +43° (*c* 1·5) (Found: C, 69·1; H, 5·8. $C_{40}H_{38}O_{11}$ requires C, 69·1; H, 5·5%).

2,3-*Dideoxy*-4,6-*di*-O-*mesyl*-α-D-threo-*hexopyranosyl* 2,3-*Dideoxy*-4,6-*di*-O-*mesyl*-α-D-threo-*hexopyranoside* (10).—A solution of the tetrabenzoate (8) (1·2 g) in dichloromethane (20 ml) was treated with dry methanol containing a trace of sodium methoxide. The mixture was stored at room temperature for 6 h and then allowed to percolate through a short column of silica gel which was then washed well with dichloromethane–methanol (2 : 1) and the resulting solution was evaporated to dryness to give the tetradeoxy-disaccharide (9), which did not crystallise. The syrup was dissolved in pyridine and cooled to 0°, and mesyl chloride (2 ml) was added; the mixture was left at room temperature

[10] N. J. M. Birdsall, *Tetrahedron Letters*, 1971, 2675.

[11] C. L. Stevens, P. Blumberg, and D. L. Wood, *J. Amer. Chem. Soc.*, 1964, **86**, 3592; A. B. Foster, R. Harrison, J. Lehmann, and J. M. Webber, *J. Chem. Soc.*, 1963, 4471.

for 3 h. The solid obtained by pouring the mixture into ice–water was filtered off, dissolved in a little dichloromethane, and applied to the top of a dry-packed column of silica gel. The column was initially eluted with dichloromethane (250 ml) to get rid of some impurities, and then eluted with dichloromethane–ethanol (20 : 1; 500 ml) to give the *tetrasulphonate*, which was recrystallised from dichloromethane–propan-2-ol (yield 0·7 g, 70%); m.p. 70—72°, $[\alpha]_D$ +76° (*c* 0·5) (Found: C, 32·7; H, 5·1; S, 22·2. $C_{16}H_{30}O_{15}S_4$ requires C, 32·5; H, 5·1; S, 21·7%).

2,3,6-*Trideoxy*-6-*iodo*-4-O-*mesyl*-α-D-erythro-*hexopyranosyl* 2,3,6-*Trideoxy*-6-*iodo*-4-O-*mesyl*-α-D-erythro-*hexopyranoside* (4).—A solution of the tetramesylate (3) (2 g) and anhydrous sodium iodide (4 g) in anhydrous acetone (200 ml) was heated under reflux for 48 h. The inorganic precipitate was filtered off and the filtrate evaporated to dryness. The resulting solid residue was partitioned between dichloromethane and dilute aqueous sodium thiosulphate, and the organic layer was washed twice with water and concentrated to dryness. Recrystallisation of the residue from dichloromethane–propan-2-ol gave the 6,6′-*di-iodide* (2·0 g, 90%), m.p. 201—203°, $[\alpha]_D$ +114° (*c* 1) (Found: C, 26·1; H, 4·0; S, 9·5. $C_{14}H_{24}I_2O_9S_2$ requires C, 25·7; H, 3·7; S, 9·8%).

2,3,6-*Trideoxy*-4-O-*mesyl*-α-D-erythro-*hexopyranosyl* 2,3,6-*Trideoxy*-4-O-*mesyl*-α-D-erythro-*hexopyranoside* (5).—A mixture of the 6,6′-di-iodo-derivative (4) (3 g), barium carbonate (10 g), and Raney nickel (one spatula load) in ethanol (200 ml) was heated under reflux and stirred vigorously while hydrazine hydrate (10 ml) was added dropwise during about 10 min. The mixture was then heated under reflux for a further 2 h, filtered through Hyflo-supercel, and then evaporated to dryness. The residue was partitioned between dichloromethane and dilute aqueous sodium thiosulphate and the organic layer was separated, washed well with water, dried ($MgSO_4$), and evaporated to dryness. Recrystallisation of the residue from dichloromethane–propan-2-ol gave the *hexadeoxy-dimesylate* (1·3 g, 71%), m.p. 113—115°, $[\alpha]_D$ +160° (*c* 0·9) (Found: C, 41·3; H, 6·5; S, 16·3. $C_{14}H_{26}O_9S_2$ requires C, 41·8; H, 6·5; S, 15·9%).

4-*Acetamido*-2,3,4,6-*tetradeoxy*-α-D-threo-*hexopyranosyl* 4-*Acetamido*-2,3,4,6-*tetradeoxy*-α-D-threo-*hexopyranoside* (13).—A mixture of the 4,4′-dimesylate (5) (0·3 g) and sodium azide (0·3 g) in hexamethylphosphoric triamide (2 ml) was maintained at 85° (oil-bath) for 12 h and then poured into water. The precipitated syrup was extracted from the mixture with ether (3 × 25 ml) and the extract was washed well with water, dried ($MgSO_4$), and evaporated to a clear syrup of the diazide (11) which could not be crystallised. The diazide was dissolved in ethanol (50 ml), a little Raney nickel was added, and the mixture was maintained at reflux while hydrazine hydrate (3 ml) was added slowly during 15 min. The mixture was heated under reflux for a further 1 h, filtered through Hyflo-supercel and evaporated to dryness to give the syrupy diamine (12), which did not crystallise. The syrup was then dissolved in ethanol (10 ml) and treated with acetic anhydride (0·5 ml); the mixture was left for 12 h. The product was filtered off and recrystallised from propan-2-ol to give the *diacetamido-derivative* (0·22 g, 82%), m.p. 310—312°, $[\alpha]_D$ +144° (*c* 0·25 in $Me_2N{\cdot}CHO$) (Found: C, 58·9; H, 8·9; N, 8·3. $C_{16}H_{28}N_2O_7$ requires C, 58·5; H, 8·5; N, 8·5%).

Reaction of 2,3,6-*Trideoxy*-4-O-*mesyl*-α-D-erythro-*hexopyranosyl* 2,3,6-*Trideoxy*-4-O-*mesyl*-α-D-erythro-*hexopyranoside* (5) *with Sodium Benzoate in Hexamethylphosphoric Triamide*.—A mixture of the dimesylate (5) (3·15 g) and sodium benzoate (7 g) in hexamethylphosphoric triamide (25 ml) was maintained at 100° (bath temp.) for 36 h, then poured into water. The precipitated syrup was isolated by extraction with ether (3 × 50 ml) in the usual way to give a syrup which was shown (t.l.c.) to be composed of at least two components of similar mobilities in several solvent systems. The syrupy mixture was dissolved in dry methanol containing a trace of sodium methoxide and stored at room temperature for 36 h. T.l.c. indicated that it contained two products of differing mobilities. Silica gel (8 g) was added directly to the mixture and the slurry was dried using a rotary evaporator. The resulting solid was applied to the top of a dry column of silica gel (200 g) and then eluted with dichloromethane–ethanol (25 : 1 v/v; 25 ml fractions).

The fastest moving component, contained in the early fractions, gave a syrup (1 g, 55%) of 2,3,6-trideoxy-α-D-*threo*-hexopyranosyl 2,3,4,6-tetradeoxy-α-D-glycerohex-2-enopyranoside (17) which smelt of methyl benzoate, which was also detected by its i.r. spectrum (1730 cm^{-1}). Tosylation of (17) afforded the *monotosylate* (18) (79%), m.p. 96—98° (ethanol–water), $[\alpha]_D$ +63° (*c* 0·6) (Found: C, 60·0; H, 6·5; S, 7·9. $C_{19}H_{25}O_6S$ requires C, 59·8; H, 6·7; S, 8·4%).

The fractions containing the slower moving component were evaporated to a white crystalline residue, recrystallisation of which from ethanol–light petroleum gave 2,3,6-*trideoxy*-α-D-threo-*hexopyranosyl* 2,3,6-*trideoxy*-α-D-threo-*hexopyranoside* (15) (0·6 g, 31%), m.p. 170—171°, $[\alpha]_D$ +163° (*c* 0·6 in EtOH) (Found: C, 59·2; H, 9·8. $C_{12}H_{22}O_5$ requires C, 58·6; H, 8·9%). The *dimesylate* (16) (80%) had m.p. 136—138° (from propan-2-ol), $[\alpha]_D$ +114° (*c* 0·8) (Found: C, 41·8; H, 6·4; S, 16·0. $C_{14}H_{26}O_9S_2$ requires C, 41·8; H, 6·5; S, 15·9%).

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