#### Nitrogen-containing Carbohydrate Derivatives. Part XXIX.† Derivatives of 2,6-Diamino-2,3,4,6-tetradeoxy-D-threo-hexose (epi-Purpurosamine C) ‡

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Synthesis of the title compounds has shown purpurosamine C to be 2,6-diamino-2,3,4,6-tetradeoxy-D-erythrohexose, and the diamino-sugar component of sisomicin to be 2,6-diamino-2,3,4,6-tetradeoxy-D-glycero-hex-4enose.

SEVERAL recent papers have been concerned with the structures of the gentamicin group <sup>1</sup> of aminoglycoside antibiotics. The structure of gentamicin A has been elucidated,<sup>2</sup> but the structures of the chemotherapeutically important C compounds have not been completely described. The C complex <sup>3</sup> can be separated into gentamicins C1, C2, and C1a,4,5 all of which contain the branched-chain 3-methylamino-sugar, garosamine,<sup>6-8</sup> and deoxystreptamine. The third component, a 2,6-diamino-2,3,4,6-tetradeoxyaldose, varies; these compounds have been named the purpurosamines A—C (from gentamicin  $C_1$ ,  $C_2$ , and  $C_{1^8}$ , respectively).<sup>9</sup> Amino-sugars of this type are new, both from the natural and synthetic points of view. When the present work was begun the stereochemistry of purpurosamine C (as well as of purpurosamines A and B) was unknown, and the only compound available was the diethyl dithioacetal of the 2,6-diacetamido-derivative. We therefore set out to synthesise this new type of amino-sugar, and chose as an initial target derivatives of 2,6-diamino-2,3,4,6-tetradeoxy-D-threo-hexose (1).



The approach used took advantage of the recently described work of Ferrier and his group.<sup>10</sup> The first attempted synthesis started from the known<sup>11</sup> ethyl 4,6-di-O-acetyl-2,3-dideoxy-a-D-erythro-hex-2-enopyranoside (3) [readily prepared from 3,4,6-tri-O-acetyl-Dglucal (2)] and proceeded as shown in Scheme 1, which is largely self-explanatory, to compound (4).<sup>10</sup> Attempts were then made to introduce an azido-function at

† Part XXVIII, R. D. Guthrie and R. D. Wells, Carbohydrate

*k* - *k* 

<sup>1</sup> M. J. Weinstein, G. H. Luedemann, E. M. Oden, and G. H. Wagman, 'Antibacterial Agents and Chemotherapy,' American Society for Microbiology, 1963, p. 1.

<sup>2</sup> H. Maehr and C. P. Schaffner, J. Amer. Chem. Soc., 1970, 92, 1967, 5314.

<sup>3</sup> M. J. Weinstein, G. H. Luedemann, E. M. Oden, G. H. Wagman, J. P. Rosselet, J. A. Marquez, C. T. Coniglio, W. Cherney, H. L. Herzog, and J. Black, *J. Medicin. Chem.*, 1963,

6, 463. <sup>4</sup> G. H. Wagman, E. M. Oden, and M. J. Weinstein, *Appl.* Microbiol., 1968, 16, 624.

C-6 by use of sodium azide in NN-dimethylformamide (DMF), *i.e.* to prepare compound (7). A crystalline



product, ' compound A,' was formed, but it contained no SCN, NCS, OMs, or N<sub>3</sub> groups, as indicated by its i.r. and n.m.r. spectra. Elemental analysis showed the loss



of a mesyloxy-group and the gain of three nitrogen atoms. Structures (9) and (11) appear to be most likely for compound A. Two pathways for the formation of these structures seem possible: displacement of the 6-mesyloxy-group in structure (4) to give (7), followed by 1,3-dipolar addition to the 2-isocyanate

<sup>5</sup> G. H. Wagman, J. A. Marquez, and M. J. Weinstein, J. Chromatography, 1968, **34**, 210.

<sup>6</sup> W. Meyer zur Reckendorf and E. Bischof, Tetrahedron Letters, 1970, 2475; Angew. Chem. Internat. Edn., 1971, **10**, 660. 7 D. J. Cooper, M. D. Yudis, R. D. Guthrie, and A. M. Prior,

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<sup>10</sup> R. J. Ferrier and N. Vethaviyaser, J. Chem. Soc. (C), 1971, 1907. <sup>11</sup> R. J. Ferrier and N. Prasad, J. Chem. Soc. (C), 1969, 570.

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group (Scheme 2), or 1,3-dipolar addition of the azide ion to the 2-isothiocyanate group to give compound



(10), followed by displacement of the 6-mesyloxy-group by nitrogen (Scheme 3) or sulphur (Scheme 4). It is known<sup>12</sup> that allyl isothiocyanate reacts with sodium



acetate at 140° gave the 2-acetamido-compound (5). However, it has been reported <sup>14</sup> that acetic anhydride reacts with isothiocyanates to give di-N-acyl derivatives (Scheme 5), whereas acetic acid reacts to give N-acyl derivatives (Scheme 6). We have now shown that acidfree acetic anhydride reacts with compound (4) to give the diacetylamino-compound (8), whereas when acetic acid was added to the pure anhydride the acetamidocompound (5) was formed.

## RNCS + Ac20 ----> RNAc2 + COS SCHEME 5

### RNCS + AcOH ----> RNHAc + COS

#### SCHEME 6

Direct displacement of the 6-mesyloxy-group in compound (5) occurred with sodium azide in DMF to give, in high yield, the key compound (6); no compound resulting from participation of the 2-acetamidogroup was detected.

Because of the problems surrounding the reactions of compound (4), a second route to (6) was developed in which an azido-group was introduced at C-6 in the early stages. This pathway (Scheme 7) in which all



SCHEME 7

Reagents: i, NaN<sub>3</sub>, Me<sub>2</sub>N·CHO; ii, EtOH, BF<sub>3</sub>; iii, MeONa, MeOH; iv, MsCl, pyridine; v, KSCN, Me2N·CHO2; vi, heat, toluene.

spectrum of compound A [ $\lambda_{max}$  (MeOH) 254 nm ( $\epsilon$ steps gave high yields and which started from the known 15 3,4-di-O-acetyl-6-O-tosyl-D-glucal (12), is again essentially self-explanatory.

Treatment of compound (13) with benzene-ethanol

<sup>14</sup> 'Organic Chemistry of Bivalent Sulphur,' vol. 6, ed. E. Reid, Chemical Publishing Co., New York, 1966. <sup>15</sup> T. Maki and S. Tejima, *Chem. and Pharm. Bull. (Japan)*,

1967, **15**, 1367.

- 2160)] appears to rule out structure (11). [For example, 5-ethylthiotetrazole has  $^{13}$   $\lambda_{max}$ . (MeOH) 237 nm ( $\varepsilon$ 2880).]Ferrier et al. reported <sup>10</sup> that treatment of compound
- (4) with acetic anhydride and anhydrous sodium

azide to give 1-allyltetrazole-5-thiol, and so one of the

last two postulates could be correct, though the u.v.

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in the presence of boron trifluoride gave the  $\alpha$ - and  $\beta$ -anomers of the 2-ene (14) in the ratio 4:1 (n.m.r. analysis). No method for ready separation of the anomers was found, and so further steps were carried out on the anomeric mixture. The  $\alpha$ :  $\beta$  ratio (80:20) of the anomers formed from (13) is similar to that<sup>11</sup> from 3,4,6-tri-O-acetyl-D-glucal (85:15). This similarity perhaps supports the view of Ferrier et al.<sup>11</sup> rather than that of Russian workers 16 involving participation of a 6-acetoxy-group; however the reaction of compound (13) was much slower [48 h, cf. 0.5 h for (2)]. Treatment of compound (17) with acetic anhydride and sodium acetate in the presence of acetic acid gave the expected key compound (6), identical with that prepared by Scheme 1.

Hydrogenation of the azido-group in compound (6) in the presence of Adams catalyst would not proceed unless the substrate was first stirred with Raney nickel in ethanol. This presumably removed traces of sulphur compounds which poisoned the catalyst. Acetylation of the reduced compound, and treatment with ethanethiol in hydrochloric acid gave syrupy 2,6-diacetamido-2,3,4,6-tetradeoxy- $\alpha$ -D-threo-hexose diethyl dithioacetal (18),  $[\alpha]_{\rm D}$  -30°, further characterised as its 5-0-acetyl derivative (19), also a syrup,  $[\alpha]_{D} - 19^{\circ}$ . The rotations for the corresponding purpurosamine C derivatives from gentamicin  $C_{1a}$ , both crystalline, were  $+27^{\circ}$ and  $+40.3^{\circ}$ . The foregoing synthesis establishes that purpurosamine C does not have the D- or L-threoconfiguration.

While this work was in progress Daniels and his colleagues <sup>17</sup> showed by n.m.r. and  $[\alpha]_p$  measurements on purpurosamine glycosides that they belong to the p-series. Thus purpurosamine C is firmly identified



as 2,6-diamino-2,3,4,6-tetradeoxy-D-erythro-hexose (20). Umezawa and his colleagues 18 have recently described the synthesis of the methyl glycoside of (20), but no correlation was made with purpurosamine C.

<sup>16</sup> M. F. Shostakovskii, V. M. Annekova, E. A. Gaitseva, K. F. Lavrova, and A. I. Polyakov, *Izvest. sibirsk. Otdel. Akad.* Nauk, Ser. Khim. Nauk, 1967, 163.

<sup>17</sup> P. J. L. Daniels, personal communication.

Another recently reported aminoglycoside antibiotic, sisomicin,<sup>19,20</sup> contains a 2,6-diamino-2,3,4,6-tetradeoxyhex-4-enosyl system of unknown stereochemistry. Thiolysis of dihydrosisomicin<sup>20</sup> gave a diethyl dithioacetal,  $[\alpha]_{p}$  +32.0°, characterised further as its 5-0acetyl derivative,  $[\alpha]_{D}$  +21.6°. These data and comparison of n.m.r. spectra showed that these new compounds are enantiomeric with (18) and (19), and therefore have the *L*-threo-configuration. Thus, dihydrosisomicin contains the system (21) and sisomicin itself has the partial structure (22).

#### EXPERIMENTAL

All extracts were dried over sodium sulphate; solvents were removed in vacuo below 50° on a rotary evaporator. T.l.c. and preparative layer chromatography (p.l.c.) were carried out on silica gel (Merck GF<sub>254</sub>). Optical rotation measurements (Perkin-Elmer 141) are for chloroform solutions unless otherwise stated. N.m.r. data are for solutions in deuteriochloroform.

Reaction of Ethyl 2,3,4-Trideoxy-2-isothiocyanato-6-O-(4) methylsulphonyl-a-D-threo-hex-3-enopyranoside with Sodium Azide in DMF.—Compound (4) 10 (170 mg) was heated with sodium azide (45 mg) in dry DMF (3 ml) for 1.5 h at  $80^{\circ}$ . The solution was evaporated and the solid residue extracted with hot ethyl acetate; the extract was filtered and the solvent removed. The solid product was purified by p.l.c. (10% acetone-petroleum) to give compound A (90 mg), m.p. 130–132°,  $[\alpha]_{\rm D}$  +330° (c 1 in MeOH), λ<sub>max.</sub> (MeOH) 254 nm (ε 2160); τ 3·24-3·82 (2H, m, vinylic), 4.27-4.52 (1H, m), 4.85-5.09 (1H, m), 5.18br (1H, s), 6-6.65 (3H, m), 6.7-7.1 (1H, dd, J 3.5 and 14 Hz) (Found: C, 44.9; H, 5.1; N, 23.3; S, 12.75%; m/e 241. Calc. for C<sub>9</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>S: C, 45.0; H, 5.0; N, 23.3; S, 13.35%; M, 240).

Ethyl 2-Acetamido-2,3,4-trideoxy-6-O-methylsulphonyl-a-D-threo-hex-3-enopyranoside (5).-Ethyl 2,3,4-trideoxy-2isothiocyanato-6-O-methylsulphonyl-a-D-threo-hex-3-enopyranoside (4) (1.5 g) was heated with reagent grade acetic anhydride (10 ml) and anhydrous sodium acetate (255 mg) for 4 h at 120°. The acetic anhydride was evaporated off, ice-water was added, and the product was extracted with chloroform. Removal of the solvent left an evilsmelling brown syrup (1.43 g) which was dissolved in ether. Addition of light petroleum precipitated a white solid (47%), that gave needles of the 2-acetamido-derivative (5), m.p. 89-91° (from ethyl acetate-light petroleum),  $[\alpha]_{\rm p}$  +132° (c 2) (lit.,<sup>10</sup> m.p. 90-91°);  $\tau$  3.8-4.2 (3H, m, H-3 and -4, N-H), 5.2 (1H, s, H-1), 5.48-5.96 (4H, m, H-2, -5, -6, and -6'), 6.17-6.58 (2H, m, O.CH2.CH3), 6.94 (3H, s, MeSO<sub>2</sub>), 8·2 (3H, s, MeCO), and 8·76 (3H, t, O·CH<sub>2</sub>·-CH<sub>3</sub>) (Found: C, 44.7; H, 6.5; N, 4.8. Calc. for C<sub>11</sub>H<sub>19</sub>-NO<sub>6</sub>S: C, 45.0; H, 6.5; N, 4.8%).

Repetition of this experiment on a smaller scale gave a 60% yield of pure product.

In a further experiment, compound (4) (1 g) was dissolved in acid-free acetic anhydride (7 ml) and heated at 120° for 4 h with anhydrous sodium acetate (170 mg), and

 <sup>&</sup>lt;sup>18</sup> S. Umezawa, T. Tsuchiya, and Y. Okazaki, Bull. Chem. Soc. Japan, 1971, 44, 3494.
<sup>19</sup> D. J. Cooper, R. S. Jaret, and H. Reimann, Chem. Comm.,

<sup>1971, 285.</sup> 

<sup>&</sup>lt;sup>20</sup> H. Reimann, R. S. Jaret, and D. J. Cooper, Chem. Comm., 1971, 924.

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acetic acid (0.5 ml). Work-up as before gave, after recrystallisation, compound (5) (60%), m.p. 89–90°.

Ethyl 2,3,4-Trideoxy-2-diacetylamino-6-O-methylsulphonyl-  $\alpha$ -D-threo-hex-3-enopyranoside (8).—Compound (4) (500 mg) was dissolved in acid-free acetic anhydride (4 ml), sodium acetate (85 mg) was added, and the whole was refluxed at 120° for 4 h. T.l.c. showed the presence of one major component together with at least three other components of greater  $R_{\rm F}$  values. The mixture was worked up as before. The crude product was purified by p.l.c. (chloroform) and the band of lowest  $R_{\rm F}$  value extracted to give as a yellow syrup the diacetylamino-derivative (8) (44%),  $[\alpha]_{\rm D}$  +72° (c 0.55);  $\tau$  4.22 (2H, m, H-3 and -4), 4.72 (1H, s, H-1,  $J_{1,2}$  4.5 Hz), 5.3—5.8 (4H, m, H-2, -5, -6, and -6'), 5.94—6.47 (2H, m, O·CH<sub>2</sub>CH<sub>3</sub>), 6.91 (3H, s, MeSO<sub>2</sub>), 7.58 (6H, s, NAc<sub>2</sub>), and 8.8 (3H, t, O·CH<sub>2</sub>·CH<sub>3</sub>) (Found: C, 47.2; H, 6.3; N, 4.2. C<sub>13</sub>H<sub>21</sub>NO<sub>7</sub>S requires C, 46.6; H, 6.3; N, 3.2%).

Ethyl 2-A cetamido-6-azido-2,3,4,6-tetrade $oxy-\alpha$ -D-threohex-3-enopyranoside (6).—Ethyl 2-acetamido-2,3,4-trideoxy-6-O-methylsulphonyl- $\alpha$ -D-threo-hex-3-enopyranoside

(5) (600 mg) was dissolved in dry dimethylformamide, and sodium azide (300 mg) was added. After heating at 80° for 3 h, t.l.c. showed completed reaction. The mixture was poured into ice-water to give an emulsion, which was extracted with chloroform. Recrystallisation of the solid product from cyclohexane-light petroleum gave the *product*, m.p. 71-72°,  $[\alpha]_{\rm D}$  -3° (c 2.07),  $\tau 4.0-4.5$  (3H, m, H-3 and -4 and NH), 5.27 (1H, s, H-1), 5.59 (2H, m, H-2 and -5), 6.16-7.0 (4H, m, H-6 and 6',  $O \cdot CH_2 \cdot CH_3$ ), 8.07 (3H, s, NHAc), and 8.82 (3H, t,  $O \cdot CH_2 \cdot CH_3$ ) (Found: C, 50.1; H, 6.8.  $C_{10}H_{16}N_4O_3$  requires C, 50.0; H, 6.7%).

2,6-Diacetamido-2,3,4,6-tetradeoxy- $\alpha$ -D-threo-hexose Diethyl Dithioacetal (18).—Compound (6) (100 mg) was dissolved in ethanol and stirred with excess of Raney nickel for 2 h. After filtration, Adams catalyst was added and the mixture was hydrogenated for a further 2 h. Filtration and evaporation gave a syrup which was acetylated with pyridine-acetic anhydride to give, as a syrup, ethyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-threo-hexose (116 mg);  $\tau$  5.4br (1H, s, H-1), 8.06 (6H, s, 2 × NAc), 8.21–8.76 (4H, m, H-3, -3', -4, and -4'), and 8.88 (3H, t, O.CH2.CH3). This product (110 mg) was dissolved in concentrated hydrochloric acid (0.5 ml); the solution was treated with ethanethiol (0.5 ml) and stirred vigorously overnight. The mixture was diluted with water (100 ml), neutralised with excess of lead carbonate, and freeze-dried. Reacetylation of the residue with acetic anhydride-methanol gave a sticky white solid. This was extracted with chloroform to give, as a syrup, the diethyl dithioacetal (18) (110 mg),  $[\alpha]_p - 30^\circ$  (c 0.36 in MeOH);  $\tau$  (C<sub>5</sub>D<sub>5</sub>N) 5.65 (1H, d, H-1), 7·79 (3H, s, NHAc), 7·89 (3H, s, NHAc), 7·94-8·3 (4H, m, 2  $\times$  H-3, 2  $\times$  H-4), and 8.55–8.9 (6H, six-line m, 2  $\times$ S·CH<sub>2</sub>·CH<sub>3</sub>) (Found: C, 49.7; H, 8.00. C<sub>14</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub> requires C, 50.0; H, 8.4%).

2,6-Diacetamido-5-O-acetyl-2,3,4,6-tetradeoxy-D-threo-hexose Diethyl Dithioacetal (19).—Compound (18) (50 mg) was dissolved in dry pyridine (2 ml) and acetic anhydride (3 drops) was added. The mixture was stirred at room temperature for 3 h and water was added. Evaporation to dryness gave, as a syrup, the acetal (19),  $[\alpha]_D - 19^\circ$ ;  $\tau$  (C<sub>5</sub>D<sub>5</sub>N) 5.75br (1H, d, H-1), 7.8—8.5 (13H, m, 2 × NHAc, OAc, 2 × H-3, 2 × H-4), and 8.65—9.1 (6H, m, 2 × O·CH<sub>2</sub>·CH<sub>3</sub>) (Found: C, 50.7; H, 8.0; N, 7.1. C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>S requires C, 50.8; H, 8.0; N, 7.4%).

3,4-Di-O-acetyl-6-azido-6-deoxy-D-glucal (13).—3,4-Di-O-acetyl-6-O-p-tolylsulphonyl-D-glucal (12) <sup>15</sup> (9 g) was dissolved in dry dimethylformamide (40 ml), and sodium azide (2·4 g) was added. The mixture was heated at 80° for 4 h, then poured into ice-water to give a syrup, which was extracted with chloroform. The resulting syrup (98%) was purified by column chromatography (20% petroleum-chloroform), to give, as a yellow mobile liquid, the product (13) (70%),  $[\alpha]_D - 6^\circ$  (c 1·89);  $\tau$  (CDCl<sub>3</sub>) 3·49br (1H, d, H-1,  $J_{1.2}$  6·5 Hz), 4·53—4·97 (2H, m, H-3 and -4), 4·98—5·24 (1H, dd, H-2,  $J_{2.3}$  3 Hz), 5·57—5·96br (1H, q, H-5), 6·34—6·62 (2H, m, H-6 and -6') and 8·3 (6H, d, 2 × OAc) (Found: C, 47·3; H, 5·4; N, 16·0. C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub> requires C, 47·1; H, 5·1; N, 16·5%).

Extensive decomposition of the remainder of the product occurred on the column. A reaction on half the scale gave a yield of 86%.

Ethyl 4-O-Acetyl-6-azido-2,3,6-trideoxy-D-erythro-hex-2enopyranoside (14).-3,4-Di-O-acetyl-6-azido-6-deoxy-Dglucal (13) ( $2\cdot 2$  g) was dissolved in benzene (17 ml) containing ethanol ( $1\cdot 4$  ml); boron trifluoride-ether ( $0\cdot 7$  ml) was added and the mixture was stirred at room temperature for 48 h. A black mobile liquid was thrown out of solution (t.l.c. showed completed reaction).

The excess of acid catalyst was neutralised with sodium carbonate and the solids and solvent were removed to give a black syrup. This was purified on alumina (chloroform) to give an orange mobile liquid (2·1 g, ca. 100%) which was a 4:1 mixture of the  $\alpha$ - and  $\beta$ -anomers of ethyl 4-O-acetyl-6-acido-2,3,6-trideoxy-D-erythro-hex-2-enopyranoside (14) (by integration of the vinylic proton signals at  $\tau$  4·15 and 4·08, respectively) (Found: C, 49·4; H, 6·2; N, 16·9. C<sub>10</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub> requires C, 49·8; H, 6·3; N, 17·4%).

In a larger scale experiment (4 g), a small amount of starting material remained. This was removed by column chromatography (with 20% ethyl acetate-cyclohexane).

6-Azido-2,3,6-trideoxy-D-erythro-hex-2-enopyrano-Ethyl side.—Ethyl 4-O-acetyl-6-azido-2,3,6-trideoxy-D-erythrohex-2-enopyranoside (14) (2 g) was dissolved in dry methanol (100 ml) containing sodium (ca. 6 mg). The mixture was stirred overnight, excess of sodium methoxide was destroyed with carbon dioxide, and the solution was evaporated. Extraction with hot ethyl acetate gave a yellow mobile liquid. This was purified on silica (20%)ethyl acetate-benzene) to give the product (90%),  $[\alpha]_{D}$  $-20^{\circ}$  (c 2.085 in MeOH);  $\tau$  3.94–4.33 (2H, m, H-2 and -3), 5br (1H, s, H-1), 5.74-6.62 (6H, m, H-4, -5, -6, and -6' and O·CH2·CH3), 7·78-8·4br (1H, s, OH, disappeared on addition of D<sub>2</sub>O), and 8.72 (3H, t, O·CH<sub>2</sub>CH<sub>3</sub>) (Found: C, 48.7; H, 6.6; N, 20.7. C<sub>8</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub> requires C, 48.2; H, 6.6; N, 21.0%).

Ethyl 6-Azido-2,3,6-trideoxy-4-O-methylsulphonyl-Derythro-hex-2-enopyranoside (15).—The previous compound (860 mg) was dissolved in dry pyridine (10 ml) and cooled to 0°; methanesulphonyl chloride (0.5 ml) was added and the mixture was kept at 0° for 15 h. Work-up in the usual manner gave a yellow syrup (75%), which crystallised from light petroleum to give needles of the product (15), m.p. 48—49°,  $[\alpha]_{\rm D}$  +44° (c 2·0);  $\tau$  3·84— 4·12 (2H, m, H-2 and -3), 4·72—5·4 (2H, m, H-1 and -4), 5·74—6·6 (5H, m, H-5, -6, and -6' and O·CH<sub>2</sub>·CH<sub>3</sub>), 6·94 (3H, s, MeSO<sub>2</sub>), and 8·72 (3H, t, O·CH<sub>2</sub>·CH<sub>3</sub>) (Found: C, 39·2; H, 5·3; N, 14·8. C<sub>9</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>S requires C, 39·0; H, 5·5; N, 15·2%).

Ethyl 6-Azido-2,3,4,6-tetradeoxy-2-isothiocyanato-D-threo-

hex-3-enopyranoside (17).-Ethyl 6-azido-2,3,6-trideoxy-4-O-methylsulphonyl-a-D-erythro-hex-2-enopyranoside (15)(250 mg) was dissolved in dry dimethylformamide (5 ml) and potassium thiocyanate (300 mg) was added. The mixture was stirred at room temperature for 4 days, then poured into ice-water to give an emulsion; this was extracted with chloroform to give a syrup, whose i.r. spectrum showed the presence of thiocyanate (ca. 2170 cm<sup>-1</sup>) and isothiocyanate (2050 cm<sup>-1</sup>) groups. Isolation 6-azido-2,3,6-trideoxy-4-thiocyanato-a-D-threoof ethyl hex-2-enopyranoside (16) was not attempted. The syrup was taken up in toluene and heated for 1 h at 100°. Evaporation gave a yellow mobile liquid which was purified by p.l.c. (10% ethyl acetate-benzene), to give the isothiocyanate (17) (70%),  $[\alpha]_{\rm D}$  –381° (c 1.65);  $\tau$  4.2 (2H, m, H-3 and -4), 4.95 (1H, narrow d, H-1, J ca 1 Hz), 5.44-5.77 (1H, m, H-2 or -5), 5.94-6.4 (3H, m, H-2 or -5 and O·CH2·CH3), 6·42-6·67 (2H, m, H-6 and -6'), and 8·73 (3H, t,  $O \cdot CH_2CH_3$ ) (Found: C, 45.4; H, 5.1; N, 22.7.  $C_9H_{12}N_4O_2S$  requires C, 45.0; H, 5.0; N, 23.3%).

Ethyl 2-Acetamido-6-azido-2,3,4,6-tetradeoxy- $\alpha$ -D-threohex-3-enopyranoside (6).—Compound (17) (145 mg), toluene (5 ml), acetic anhydride (1 ml), and acetic acid (0.5 ml), together with anhydrous sodium acetate, were heated at 140° for 4 h. The mixture was extracted with chloroform and the crude product purified by p.l.c. (chloroform) to give a syrup which crystallised from cyclohexane-light petroleum to give the *product* (6), m.p. 71—72°,  $[\alpha]_{\rm D}$  —3°, identical with the sample already prepared.

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