Syntheses of Derivatives of 2,6-Diamino-2,3,4,6-tetradeoxy-DL-*erythro*-hexose (DL-Purpurosamine C) and 2,6-Diamino-2,3,4,6-tetradeoxy-DL-*threo*-hexose (*epi*-DL-Purpurosamine C)

By **John S. Brimacombe,* Ibrahim Da'aboul,** and **Leslie C. N. Tucker,** Chemistry Department, The University, Dundee DD1 4HN

Addition of nitrosyl chloride to 2-acetoxymethyl-3,4-dihydro-2*H*-pyran (7) yielded a dimeric adduct (8), which was converted into methyl 6-*O*-acetyl-3,4-dideoxy-α-DL-*glycero*-hexopyranosid-2-ulose oxime (9) on treatment with methanol in the presence of pyridine. Catalytic reduction of the oxime (9), followed by acetylation of the resulting amine, gave a separable mixture of methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-DL-*erythro*-hexopyranoside (11) (56%) and the corresponding *threo*-isomer (12) (20%). These compounds were transformed into the methyl glycosides (17) and (22) of DL-purpurosamine C (2,6-diamino-2,3,4,6-tetradeoxy-DL-*erythro*-hexose) and *epi*-DL-purpurosamine C (2,6-diamino-2,3,4,6-tetradeoxy-DL-*threo*-hexose), respectively, on replacement of the 6-acetoxy-group in each by an acetamido-group.

THE broad spectrum antibiotic complex gentamicin C [1] has been shown [2,3] to contain three closely related, non-reducing pseudotrisaccharides named gentamicins C_1, C_2, and C_{1a}. Each of these contains the branched-chain amino-sugar garosamine [4-6] and deoxystreptamine,[5] but each contains a different third component, a 2,6-diamino-2,3,4,6-tetradeoxyaldose;[7] these sugars have been named purpurosamines A, B, and C from gentamicins C_1, C_2, and C_{1a}, respectively. Although the gross structures and relationships between purpurosamines A (1), B (2), and C (3) were known [5] at the commencement of our studies, no stereochemical assignments had been made. However, Guthrie and Williams [8] have since prepared derivatives of the C-2 epimer of purpurosamine C that permitted the natural sugar to be assigned absolute stereochemistry and to be identified as 2,6-diamino-2,3,4,6-tetradeoxy-D-*erythro*-hexose (4). Methyl purpurosaminide C has recently been synthesized [9] from derivatives of neamine C,[10] obtained from the neomycin and kanamycin antibiotics, but no correlation was made with the natural sugar. Another aminoglycoside antibiotic, sisomicin, has recently been demonstrated [11,12] to contain a 2,6-diamino-2,3,4,6-tetradeoxyhex-4-enose, which afforded a glycosidically linked 2,6-diamino-2,3,4,6-tetradeoxy-β-L-*threo*-hexopyranoside on catalytic reduction of the carbon–carbon double bond.

Investigations in our laboratory have been primarily concerned with a synthetic approach that, with suitable modifications, might yield all three purpurosamines. In this regard, the chiral unsaturated (*S*)-aldehyde (5) was considered to possess most of the structural features sought in a progenitor of the purpurosamines, particularly as Grignard additions, *etc.* to the aldehydic function would permit extension of the side-chain necessary for syntheses of the heptoses purpurosamines A and B. Since the racemic form of (5) is readily available [13] from dimerization of acrylaldehyde, exploratory experiments were conducted with racemic 3,4-dihydro-2*H*-pyran-2-carbaldehyde, whose conversion into derivatives of DL-purpurosamine C and *epi*-DL-purpurosamine C forms the subject of the present paper.

Reduction of the racemic dimer (5) † with sodium borohydride in methanol, followed by acetylation of the resulting alcohol [14] (6), afforded 2-acetoxymethyl-3,4-dihydro-2*H*-pyran [15] (7). Addition of nitrosyl chloride in methylene chloride (or ether) across the double bond of the latter compound gave an unstable, crystalline dimer (8) of 6-*O*-acetyl-2,3,4-trideoxy-2-nitroso-α-DL-*erythro*-hexopyranosyl chloride.‡ The stereochemistry of the dimeric adduct (8) was inferred from the extensive work of Lemieux and his colleagues [16,17] on the addition of nitrosyl chloride to acetylated D-glycals. These workers have shown that the additions are *cis* and regiospecific, the product invariably being the 2-nitroso-α-D-chloro-derivative, although exceptionally *cis*-addition to

† Only one of the enantiomers is shown in the formulae, but the relative stereochemistry of the substituents is as depicted.

‡ This and successive compounds are named in accordance with accepted carbohydrate nomenclature in order to bring out the relationship with purpurosamine C.

[1] M. J. Weinstein, G. H. Luedemann, E. M. Oden, and G. H. Wagman, 'Antibacterial Agents and Chemotherapy,' American Society for Microbiology, 1963, p. 1.

[2] 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; G. H. Wagman, J. A. Marquez, and M. J. Weinstein, *J. Chromatog.*, 1968, **34**, 210.

[3] D. J. Cooper, H. Marigliano, M. D. Yudis, and T. Traubel, *J. Infectious Diseases*, 1969, **114**, 342.

[4] D. J. Cooper, M. D. Yudis, R. D. Guthrie, and A. M. Prior, *J. Chem. Soc.* (*C*), 1971, 960.

[5] D. J. Cooper, P. J. L. Daniels, M. D. Yudis, H. M. Marigliano, R. D. Guthrie, and S. T. K. Bukhari, *J. Chem. Soc.* (*C*), 1971, 3126.

[6] W. Meyer zu Reckendorf and E. Bischof, *Tetrahedron Letters*, 1970, 2475; *Chem. Ber.*, 1972, **105**, 2546.

[7] D. J. Cooper, M. D. Yudis, H. M. Marigliano, and T. Traubel, *J. Chem. Soc.* (*C*), 1971, 2876.

[8] R. D. Guthrie and G. J. Williams, *Chem. Comm.*, 1971, 923; *J.C.S. Perkin I*, 1972, 2619.

[9] S. Umezawa, T. Tsuchiya, and Y. Okazaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 3494.

[10] H. Weidmann and H. K. Zimmerman, *Annalen*, 1961, **644**, 127.

[11] D. J. Cooper, R. S. Jaret, and H. Reimann, *Chem. Comm.*, 1971, 285.

[12] H. Reimann, R. S. Jaret, and D. J. Cooper, *Chem. Comm.*, 1971, 924.

[13] F. Alder and E. Rüden, *Ber.*, 1941, **74**, 320, 905.

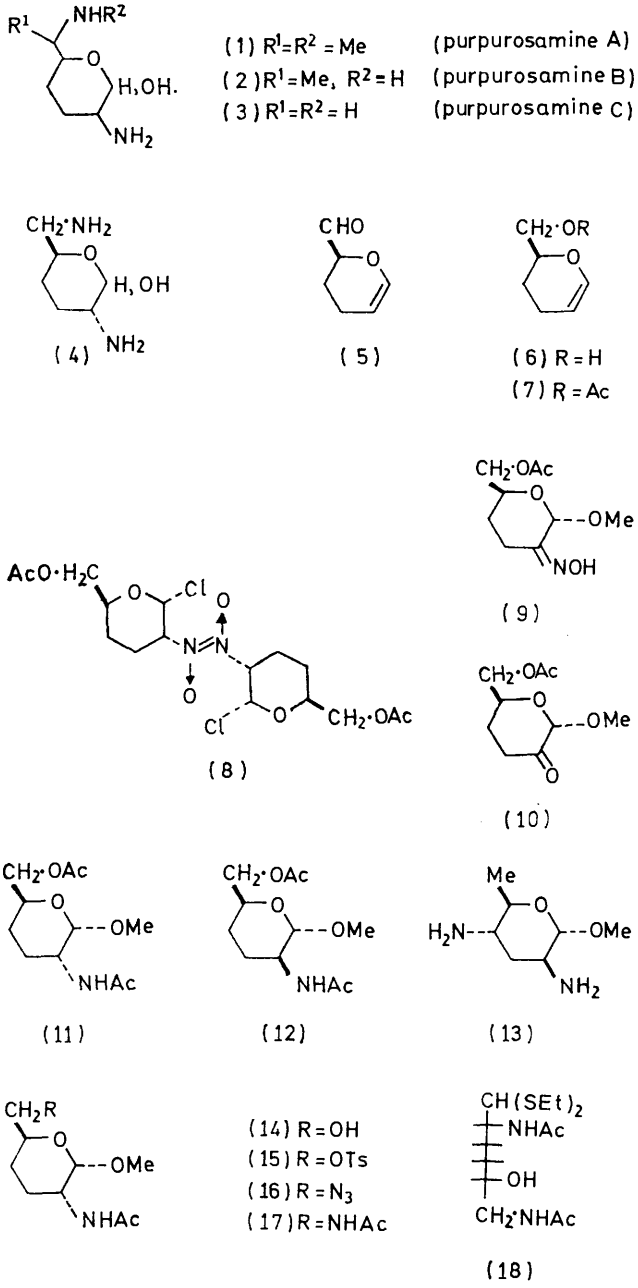
[14] F. Sweet and R. K. Brown, *Canad. J. Chem.*, 1968, **46**, 2289.

[15] R. Zelinski, A. Verbiscar, and H. J. Eichel, *J. Org. Chem.* 1950, **23**, 184.

[16] R. U. Lemieux, T. L. Nagabhushan, and I. K. O'Neill, *Tetrahedron Letters*, 1964, 1909; *Canad. J. Chem.*, 1968, **46**, 413; R. U. Lemieux, T. L. Nagabhushan, and S. W. Gunner, *ibid.*, p. 405.

[17] R. U. Lemieux and T. L. Nagabhushan, *Methods Carbohydrate Chem.*, 1972, **6**, 487.

give the β-chloro-anomer has been claimed.[18] The n.m.r. spectrum of the adduct (8) exhibited a signal for the anomeric proton as a doublet ($J_{1,2}$ *ca.* 3 Hz) at τ 3·10, which is compatible [16] with the stereochemistry assigned.



On treatment with methanol in the presence of pyridine, the nitrosyl chloride adduct (8) was smoothly converted into the α-glycosidulose oxime (9) in high yield. The structure of the oxime was originally inferred by analogy with Lemieux's work,[16,17] but the compound has since been found to be indistinguishable (by ^{1}H n.m.r. spectroscopy) from the product obtained [19] by formation of the oxime of optically pure methyl 6-*O*-acetyl-3,4-dideoxy-α-D-*glycero*-hexopyranosid-2-ulose (10); compound (10) was prepared by an unequivocal route that involved oxidation of methyl 6-*O*-acetyl-3,4-dideoxy-α-D-*erythro*-hexopyranoside with ruthenium tetroxide. In both cases, only one form of the oxime (9) appeared to be produced; this was tentatively assigned the *anti*-configuration since the n.m.r. signal of the anomeric proton is moved downfield by only *ca.* 0·4 p.p.m. from that of the ketone (10); much greater shifts (>0·9 p.p.m.) are experienced [20] by equatorially oriented protons opposing oxime hydroxy-groups in the *syn*-configuration.

Catalytic reduction of the oxime (9), followed by acetylation of the resulting amine, gave principally two products, identified as methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-DL-*erythro*-hexopyranoside (11) (56%)

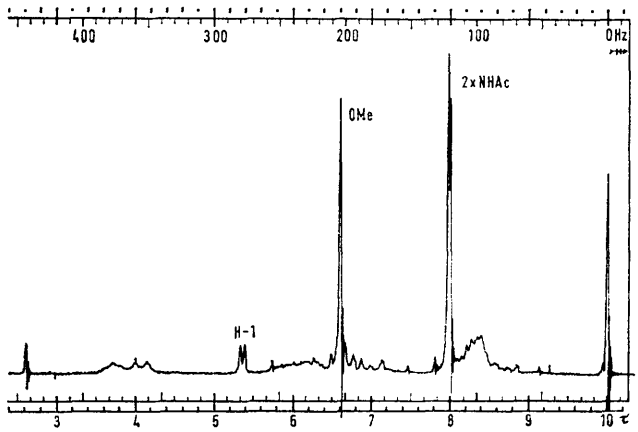


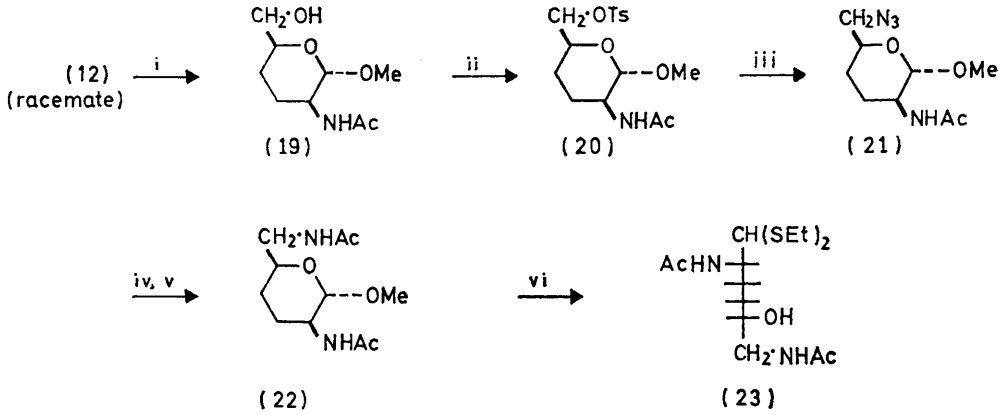
FIGURE 1 The n.m.r. spectrum ($CDCl_3$; 60 MHz) of methyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-DL-*erythro*-hexopyranoside (17)

and methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-DL-*threo*-hexopyranoside (12) (20%). The small H-1,H-2 couplings observed in the n.m.r. spectra of (11) ($J_{1,2}$ 3·2 Hz) and (12) (2·1 Hz) were in accord with the *cis* (*eq,ax*) and *trans* (*eq,eq*) arrangements, respectively, of these hydrogen atoms; the H-1,H-2 spacing observed for the *erythro*-isomer (11) is in good agreement with those reported [16,21] for a number of alkyl α-D-glucopyranosides, and that of the *threo*-isomer (12) accords with that noted for D-mannopyranosides [21] and for a related glycoside, methyl 2,4-diamino-2,3,4,6-tetradeoxy-α-DL-*arabino*-hexopyranoside [18] (13) ($J_{1,2}$ *ca.* 2 Hz).

Saponification of the 6-acetate (11) afforded the alcohol (14), which was converted into the 6-tosylate (15); this afforded methyl 2-acetamido-6-azido-2,3,4,6-tetradeoxy-α-DL-*erythro*-hexopyranoside (16) on displacement of the tosyloxy-group with azide ion in dimethyl sulphoxide. Catalytic reduction of the azide (16), followed by acetylation of the resulting amine, gave methyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-DL-*erythro*-hexopyranoside. (17). The n.m.r. spectrum (Figure 1) of the latter was

[18] Y. Suhara, F. Sasaki, G. Koyama, K. Maeda, H. Umezawa, and M. Ohno, *J. Amer. Chem. Soc.*, 1972, **93**, 6501.
[19] J. S. Brimacombe, I. Da'aboul, and L. C. N. Tucker, unpublished results.
[20] R. U. Lemieux, R. A. Earl, K. James, and T. L. Nagabhushan, *Canad. J. Chem.*, 1973, **51**, 19.
[21] R. U. Lemieux, K. James, and T. L. Nagabhushan, *Canad. J. Chem.*, 1973, **51**, 27; B. Coxon, *Tetrahedron*, 1965, **21**, 3481.

indistinguishable from that of methyl α-purpurosaminide C, thus substantiating [8] the configurational assignments made for the compounds in this series. Thiolysis of the pure D-enantiomer of the oxime (9) has been prepared by an alternative route [19] and its conversion into derivatives of natural purpurosamine C is in progress.



SCHEME Reagents: i, basic resin; ii, TsCl–C_5H_5N; iii, NaN_3–Me_2SO; iv, Pd–C, H_2; v, MeOH–Ac_2O; vi, EtSH–HCl

racemic glycoside (17) with ethanethiol in hydrochloric acid afforded crystalline 2,6-diacetamido-2,3,4,6-tetradeoxy-DL-*erythro*-hexose diethyl dithioacetal (18), whose n.m.r. spectrum showed the expected correspondence with that of the same derivative [7] obtained from natural purpurosamine C.

An identical sequence of reactions applied to the isomeric 6-*O*-acetate (12) (Scheme) afforded crystalline methyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-DL-*threo*-hexopyranoside (methyl α-DL-*epi*-purpurosaminide C) (22). Although the corresponding derivative was not available from dihydrosisomicin [11,12] for direct comparison, the n.m.r. spectrum (Figure 2) of the racemic glycoside (22) was clearly distinguishable from those of methyl α- and β-purpurosaminides C, thereby providing reasonable assurance that the structure assigned is correct.* Thiolysis of the glycoside (22) with ethanethiol in concentrated hydrochloric acid gave syrupy 2,6-diacetamido-2,3,4,6-tetradeoxy-DL-*threo*-hexose diethyl dithioacetal (23), whose n.m.r. spectrum was indistinguishable from that of the corresponding *epi*-purpurosamine C derivative. As would be expected, however, only slight differences are observed in the n.m.r. spectra of the isomeric dithioacetals (18) and (23), so that rigorous assignments of structure based solely on these derivatives did not seem justified in the absence of optical rotation data (*cf.* ref. 8).

So far we have been unable to resolve any of the compounds [*e.g.* (14) or (19)] in the two series of racemates. However, as already indicated, the optically

* *Note added in proof:* Recent investigations in our laboratories have indicated that formation and reduction of the oxime (9) are more complex than we believed at first. In particular, doubts have been raised concerning the α-configuration assigned to the *threo*-glycosides (see Scheme), although the relative stereochemistry of the substituents at C-2 and C-5 is not in question. The difficulties of assigning the anomeric configuration to glycopyranosides bearing an axial C-2 substituent (*e.g.* mannopyrannosides) by ^1H n.m.r. spectroscopy are well known. It is hoped that work in progress will clarify this situation.

EXPERIMENTAL

T.l.c. was performed on Kieselgel G, and detection was effected with vanillin–sulphuric acid.[22] I.r. spectra were

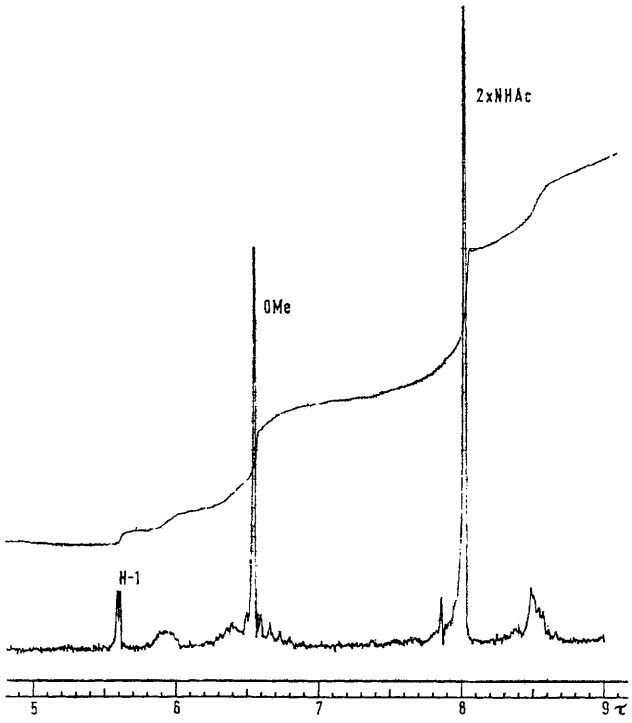


FIGURE 2 The n.m.r. spectrum ($CDCl_3$; 100 MHz) of methyl 2,6-diacetamido-2,3,4,6-tetradeoxy-α-DL-*threo*-hexopyranoside (22)

usually recorded for Nujol mulls with a Perkin-Elmer Infracord spectrophotometer and n.m.r. spectra for solutions in deuteriochloroform with 1% tetramethylsilane as internal standard using either a Perkin-Elmer R10 (60 MHz) or Varian HA-100 spectrometer. Optical rotations were measured at ambient temperature with a Perkin-Elmer 141

[22] 'Chromatography,' E. Merck AG, Darmstadt, 2nd edn., p. 30.

automatic polarimeter. Light petroleum refers to the fraction having b.p. 60—80°.

Addition of Nitrosyl Chloride to 2-Acetoxymethyl-3,4-dihydro-2H-pyran (7).—A stirred solution of the unsaturated compound (7) [15] [5·7 g; $\nu_{max.}$ (film) 1750 (C=O) and 1650 cm^{-1} (C=C)] in dry methylene chloride (50 ml) was cooled to *ca.* −25° before a pre-cooled solution of nitrosyl chloride (*ca.* 4·8 g) was added gradually. The blue-green solution was kept at −25° for a few minutes, then concentrated to near dryness; cold methanol (50 ml) was added and the solution was concentrated again until white crystals started to appear. The solution was then stored in the refrigerator for 3 h, and the white *dimeric adduct* (8) of 6-O-*acetyl*-2,3,4-*trideoxy*-2-*nitroso*-α-DL-erythro-*hexopyranosyl chloride* (4·8 g, 60%), m.p. 113—115° (decomp.), was filtered off. Subsequent reactions were carried out immediately, since the adduct rapidly decomposed at room temperature. For this reason, a satisfactory elemental analysis could not be obtained, but the n.m.r. spectrum showed signals at τ 3·10 (1H, d, $J_{1,2}$ *ca.* 3 Hz, H-1) and 7·88 (3H, s, OAc).

The same adduct was obtained in much better yield (82%) when dry ether was used instead of methylene chloride for the addition. In this case, however, the adduct could not be kept for longer than a few minutes at room temperature.

Methyl 6-O-*Acetyl*-3,4-*dideoxy*-α-DL-glycero-*hexopyranosid*-2-*ulose Oxime* (9).—A solution of the nitrosyl chloride adduct (8) (5·8 g) in methanol (10 ml) and pyridine (20 ml) was set aside overnight at room temperature; t.l.c. (acetone–light petroleum, 1 : 1) then indicated that a single product had been formed. The solution was partitioned between chloroform (100 ml) and dilute hydrochloric acid (100 ml), and the organic layer was washed with sodium hydrogen carbonate solution and dried ($MgSO_4$). Removal of the solvent gave the *oxime* (9) (5·3 g, 81%), $\nu_{max.}$ (film) 3400br (OH) and 1730 cm^{-1} (C=O), as a clear syrup that failed to crystallize; τ 5·02 (1H, s, H-1), 6·54 (3H, s, OMe), and 7·88 (3H, s, OAc).

Methyl 2-*Acetamido*-6-O-*acetyl*-2,3,4-*trideoxy*-α-DL-erythro-*hexopyranoside* (11) *and its* threo-*Isomer* (12).—A solution of the oxime (9) (3·2 g) in methanol (30 ml) containing a suspension of 30% palladium–charcoal (*ca.* 1 g) was shaken overnight under 40 atm of hydrogen at room temperature; t.l.c. (acetone–light petroleum, 1 : 1) then showed that all the starting material had been reduced. The catalyst was filtered off and acetic anhydride (30 ml) was added to the filtrate, which was then set aside for 1 h at room temperature. Removal of the solvents, with repeated additions of toluene, left a syrup that was chromatographed on silica gel (elution with acetone–light petroleum, 1 : 1) to give first the erythro-*isomer* (11) (1·6 g, 56%), b.p. 120—122° (bath) at *ca.* 0·5 mmHg, $\nu_{max.}$ (film) 3350 (NH), 1740 (C=O), and 1640 and 1530 cm^{-1} (NHAc) (Found: C, 53·7; H, 7·7; N, 5·9. $C_{11}H_{19}NO_5$ requires C, 53·9; H, 7·7; N, 5·7%), τ 5·40 (1H, d, $J_{1,2}$ 3·2 Hz, H-1), 6·63 (3H, s, OMe), and 7·96 (6H, s, NAc and OAc). Continued elution gave the threo-*isomer* (12) (0·58 g, 20%), $\nu_{max.}$ 3350 (NH), 1730 (C=O), and 1640 and 1540 cm^{-1} (NHAc), m.p. 122—123° (from chloroform–light petroleum) (Found: C, 54·1; H, 7·7; N, 5·8%), τ 5·64 (1H, d, $J_{1,2}$ 2·1 Hz, H-1), 6·60 (3H, s, OMe), 8·00 (3H, s, OAc), and 8·09 (3H, s, NAc).

Derivatives of DL-*Purpurosamine C* (2,6-*Diamino*-2,3,4,6-*tetradeoxy*-DL-erythro-*hexose*)

Methyl 2-*Acetamido*-6-*azido*-2,3,4,6-*tetradeoxy*-α-DL-erythro-*hexopyranoside* (16).—A solution of the acetoxy-derivative (11) (1·5 g) in methanol (20 ml) was stirred with Deacidite FF-IP (HO^-) resin (*ca.* 1 g) for 1 h at room temperature, during which time complete deacetylation occurred. The resin was filtered off and the filtrate was concentrated to yield the alcohol (14) (*ca.* 1 g, 82%), $\nu_{max.}$ (film) 3400 (OH) and 1650 and 1540 cm^{-1} (NHAc), as a clear syrup.

To a solution of the alcohol (14) (0·9 g) in dry pyridine (20 ml) was added an excess of toluene-*p*-sulphonyl chloride and the solution was kept for 2 h at room temperature. Work-up in the usual manner gave the syrupy tosylate (15) (1·4 g, 81%), τ 2·40 (4H, m, aromatic), 5·42 (1H, d, $J_{1,2}$ *ca.* 3·5 Hz, H-1), 6·62 (3H, s, OMe), 7·52 (3H, s, Ar*Me*), and 7·90 (3H, s, NAc).

A stirred solution of the tosylate (0·9 g) in dimethyl sulphoxide (20 ml) containing sodium azide (0·4 g) was heated at 100° for 10 h, during which time complete reaction occurred. The cooled solution was partitioned between water (100 ml) and chloroform (3 × 100 ml), and the dried ($MgSO_4$) organic extracts were concentrated to afford the *azide* (16) (0·48 g, 68%), m.p. 133—134° (from ether–light petroleum), $\nu_{max.}$ 3200 (NH), 2100 (N_3), and 1650 and 1540 cm^{-1} (NHAc) (Found: C, 47·7; H, 6·9; N, 24·5. $C_9H_{16}N_4O_3$ requires C, 47·4; H, 7·0; N, 24·6%), τ 5·35 (1H, d, $J_{1,2}$ *ca.* 3·5 Hz, H-1), 6·62 (3H, s, OMe), and 8·10 (3H, s, NAc).

Methyl 2,6-*Diacetamido*-2,3,4,6-*tetradeoxy*-α-DL-erythro-*hexopyranoside* (*Methyl* α-DL-*Purpurosaminide C*) (17).—A solution of the azide (16) (0·18 g) in dry methanol (10 ml) containing 5% palladium–charcoal (0·2 g) was shaken with a slight overpressure of hydrogen for 3 h at room temperature. The catalyst was filtered off and the filtrate was treated with a few drops of acetic anhydride to acetylate the amine. After 1 h, the solvents were removed, with repeated additions of toluene, to give the *diamide* (17) (0·11 g, 57%), m.p. 191—192° (from acetone), as fine white needles (Found: C, 53·8; H, 8·3; N, 11·3. $C_{11}H_{20}N_2O_4$ requires C, 54·1; H, 8·2; N, 11·5%), τ 5·42 (1H, d, $J_{1,2}$ *ca.* 3·5 Hz, H-1), 6·64 (3H, s, OMe), and 8·01 and 8·04 (each 3H, s, 2 × NAc). The n.m.r. spectrum (Figure 1) of the racemate was indistinguishable from that of methyl α-D-purpurosaminide C.

2,6-*Diacetamido*-2,3,4,6-*tetradeoxy*-DL-erythro-*hexose Diethyl Dithioacetal* (18).—The glycoside (17) (0·1 g) was dissolved in concentrated hydrochloric acid (0·3 ml) and this solution was vigorously stirred with ethanethiol (0·3 ml) overnight at room temperature. The excess of ethanethiol was evaporated off, the residue was diluted with water (10 ml), and the aqueous solution was neutralized with lead carbonate and filtered. The filtrate was extracted with chloroform (5 × 50 ml), and the combined extracts were dried ($MgSO_4$) and concentrated to a syrup (96 mg), which crystallized on storage in the refrigerator. Recrystallization from chloroform–light petroleum gave the *dithioacetal* (18), m.p. 123—124° (Found: C, 50·2; H, 8·0; N, 8·0; S, 18·8. $C_{14}H_{28}N_2O_3S_2$ requires C, 50·0; H, 8·4; N, 8·3; S, 19·05%), τ (C_6D_5N) 5·63 (1H, d, H-1), *ca.* 6·40 (2H, m, H-6 and H-6′), 7·30 (4H, m, 2 × S·CH_2·CH_3), 7·87 and 7·92 (s, each 3H, 2 × NAc), and *ca.* 8·75 (6H, s overlapping t, 2 × S·CH_2·CH_3). The n.m.r. spectrum of the racemic dithioacetal was indistinguishable from that of the same derivative [7] obtained from natural purpurosamine C.

Derivatives of DL-epi-*Purpurosamine C* (2,6-*Diamino*-2,3,4,6-*tetradeoxy*-DL-threo-*hexose*)

Methyl 2-*Acetamido*-6-*azido*-2,3,4,6-*tetradeoxy*-α-DL-threo-*hexopyranoside* (21).—A solution of the acetoxy-compound

(12) (0·88 g) in methanol (10 ml) was deacetylated with Deacidite FF-IP (HO^-) resin, as described for the isomeric compound, to give the alcohol (19) (0·52 g, 71%), $\nu_{max.}$ (film) 3400br (OH) and 1650 and 1540 cm^{-1} (NHAc), as a syrup. The alcohol was then converted into a syrupy tosylate (20) in 85% yield by the usual method.

Finally, the tosylate (20) (0·75 g) was transformed into the *azide* (21) (0·41 g, 82%), m.p. 106—107° (from ether–light petroleum), $\nu_{max.}$ 3200 (NH), 2100 (N_3) and 1640 and 1550 cm^{-1} (NHAc), essentially as described for the isomeric compound (Found: C, 47·1; H, 6·9; N, 24·5. $C_9H_{14}N_4O_3$ requires C, 47·4; H, 7·0; N, 24·6%).

Methyl 2,6-*Diacetamido*-2,3,4,6-*tetradeoxy*-α-DL-threo-*hexopyranoside* (*Methyl* α-DL-epi-*Purpurosaminide C*) (22).—The *diamide* (22) (0·265 g, 80%), m.p. 170—171° (from acetone), was obtained (as before) by catalytic reduction of the azide (21) (0·3 g) followed by acetylation of the resulting amine (Found: C, 54·3; H, 7·9; N, 11·2. $C_{11}H_{20}N_2O_4$ requires C, 54·1; H, 8·2; N, 11·5%). The n.m.r. spectrum (Figure 2) exhibited signals at τ 5·60 (1H, d, $J_{1,2}$ *ca.* 2Hz, H-1), 6·54 (3H, s, OMe), and 8·01 (6H, s, 2 × NAc).

2,6-*Diacetamido*-2,3,4,6-*tetradeoxy*-DL-threo-*hexose Diethyl Dithioacetal* (23).—The *racemic dithioacetal* (23) (0·16 g, 61%) was obtained as a syrup following thiolysis of the glycoside (22) (0·19 g) as described previously (Found: C, 49·4; H, 8·2; N, 7·8. $C_{14}H_{28}N_2O_3S_2$ requires C, 50·0; H, 8·4; N, 8·3%), τ (C_5D_5N), 5·62 (1H, d, H-1), 6·45 (2H, m, H-6 and H-6′), 7·30 (4H, m, 2 × S·CH_2·CH_3), 7·88 and 7·95 (s, each 3H, 2 × NAc), and 8·75 (6H, s overlapping t, 2 × S·CH_2·CH_3). Although the n.m.r. spectrum revealed the presence of small amounts of impurities, it was the same in all essential features as that of D-*epi*-purpurosamine diethyl dithioacetal.[8]

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