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THE SYNTHESIS OF RACEMIC PURPUROSAMINE B*

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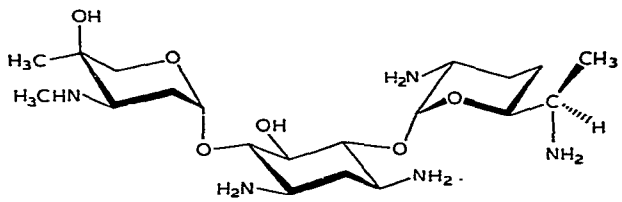
ABSTRACT

2,6-Diacetamido-2,3,4,6,7-pentadeoxy-DL-*ribo*-heptopyranose (2,6-di-*N*-acetyl-DL-purpurosamine B) was synthesized from 6-acetyl-2-methoxy-5,6-dihydro-2*H*-pyran in nine steps. The synthesis confirmed the *ribo* configuration of the natural sugar.

INTRODUCTION

Purpurosamine B is one of the two sugar components of the aminoglycosidic antibiotic gentamycin C_2 (**1**)[1] (garosamine is the other component). The constitution of purpurosamine B as a 2,6-diamino-2,3,4,6,7-pentadeoxyheptopyranose was derived from mass-spectral data[2]; its D-*ribo* configuration was determined[3] from optical rotation and ^{1}H-n.m.r. data of methyl α- and β-purpurosaminides B. We now report the first total synthesis** of DL-purpurosamine B, starting from 6-acetyl-2-methoxy-5,6-dihydro-2*H*-pyran[5] (**2**).



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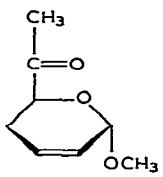

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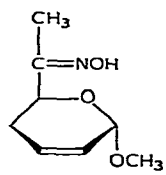

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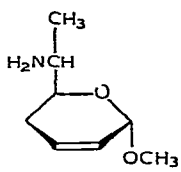

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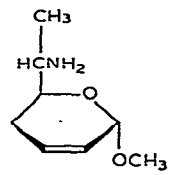

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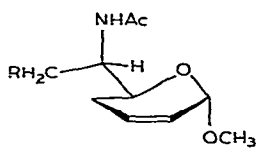
*Dedicated to Professor Roy L. Whistler.

**For the sake of simplicity, the formulae refer only to the D series.

RESULTS AND DISCUSSION

Oximation of **2** to give **3**, followed by reduction, gave two stereoisomeric amines (**4** and **5**) which were isolated as the *N*-acetyl derivatives (**6** and **7**) by chromatography and assigned *α-erythro* and *β-threo* configurations, respectively, on the basis of similarity of chemical and spectral data to those of the homologous compounds **8** and **9** obtained earlier by an analogous method from 2-methoxy-6-propionyl-5,6-dihydro-2*H*-pyran[6]. The *α-erythro* configuration of **8** was unequivocally established by its conversion into methyl 7-deoxy-α-DL-lincosaminide[6]. Compounds **6** and **8** were the major products of reduction of the corresponding oximes. They displayed similar t.l.c. behaviour: lower R_F values compared with those of **7** and **9** (see Experimental). The stereochemical analogy of the pairs **6** and **8**, and **7** and **9** was further reflected in the similarity of their ^{13}C-n.m.r. spectra (Table I). Particularly significant are the chemical shifts of C-7: in each *erythro* compound, these signals are shifted upfield 2–3 p.p.m. compared with those of the *threo* isomers. We assume that this upfield shift is due to the antiperiplanar arrangement of C-7/C-6/C-5/O-5 in the preponderating type-A conformation of **6** and **8**.



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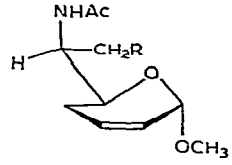


B

6 R = H
8 R = CH_3

7 R = H
9 R = CH_3

According to Eliel *et al.*[7], such an arrangement causes characteristic upfield shifts of ^{13}C-resonances, *i.e.*, C-7 in this case. It is noteworthy that an analogous

TABLE I

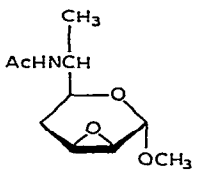
^{13}C-N.M.R. CHEMICAL SHIFTS[a] OF **6–11** AND **18**

	C-1	*C-2*[b]	*C-3*[b]	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*
6	96.21	128.57	125.46	27.05	69.16	47.64	15.46	—
7	96.07	128.86	125.23	27.47	68.97	47.35	18.38	—
8	96.15	128.80	125.41	27.45	68.71	53.80	23.35	10.21
9	96.09	128.99	125.23	27.43	67.17	53.06	25.41	10.60
10	96.69	49.01	49.75	25.41	66.16	47.33	14.69	—
11	95.89	— 50.94 —		27.57	67.52	47.53	16.44	—
18	96.64	48.92	49.80	25.63	66.21	46.84	18.12	—

[a]Resonance signals of OMe and AcO occurred in the spectra of all four compounds at 55 ± 0.5, 23.5 ± 1.5, and 169.5 ± 0.5 p.p.m., respectively. [b]Assignments may be reversed.

difference in the ^{13}C-n.m.r. shift of C-7 is also observed in the spectra of epoxides **10** and **18**, indicating the same conformation of the side-chain in these derivatives.

The type-A conformation for **6** is further supported by the ^{1}H-n.m.r. value $J_{5,6}$ 4.5 Hz. The same coupling constant for **7** is 2.5 Hz, which is indicative of the prevailing B conformation of both *β-threo* compounds **7** and **9**. The dependence of *gauche* vicinal-coupling constants on the electronegativity of substituents has been investigated[8,9].



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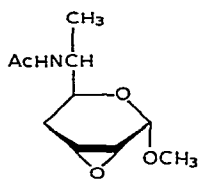

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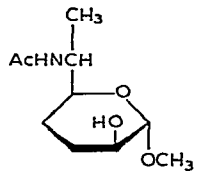

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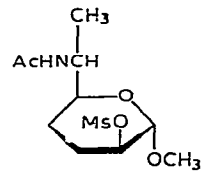

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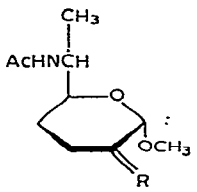
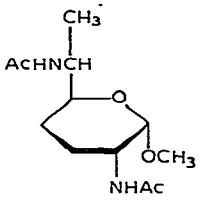


14 R = O
15 R = NOH



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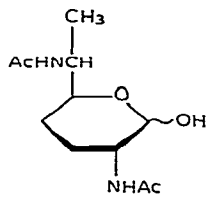

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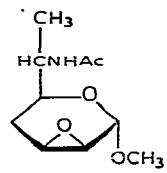

18

Epoxidation of **6** with *m*-chloroperoxybenzoic acid afforded a mixture of the *α-manno* (**10**) and *α-allo* epoxide (**11**) in the ratio 2.7 : 1. It is interesting to note that epoxidation of stereoisomer **7** under the same conditions gave only the *β-gulo* epoxide **18**.

Reduction of **10** with lithium aluminium hydride occurred cleanly and gave methyl 6-acetamido-3,4,6,7-tetradeoxy-α-DL-*arabino*-heptopyranoside (**12**). An attempt to obtain a 2-azido-2-deoxy compound from **12** *via* reaction of the mesyl derivative **13** with sodium azide failed; elimination occurred, affording **6**.

Compound **12** was oxidized with methyl sulphoxide–dicyclohexylcarbodi-imide or ruthenium tetraoxide to give ketone **14**, which was converted into the oxime **15**. Reduction of **15** with lithium aluminium hydride, followed by acetylation, afforded a crystalline diacetamido compound (26.7%) which was assigned the structure methyl 2,6-diacetamido-2,3,4,6,7-pentadeoxy-α-DL-*ribo*-heptopyranoside (**16**).

The electron-impact mass spectra (17 and 70 eV) of **16** and of methyl 2,6-di-*N*-acetyl-β-D-purpurosaminide B (**19**) were identical, except for minor differences in the intensities of some lines. The i.r. spectra were not identical, thus confirming differences in anomeric configuration.

Hydrolysis of **16** with 50% aqueous trifluoroacetic acid gave a product which was identical with authentic purpurosamine B obtained from the methyl β-glycoside (**19**) in the same way.

The synthesis presented here confirmed the *ribo* configuration of natural purpurosamine B proposed by Daniels[4].

EXPERIMENTAL

M.p.s. are uncorrected. T.l.c. was performed on Merck Silica Gel G and column chromatography on silica gel (Merck, 250–400 mesh). ^{1}H-N.m.r. spectra were recorded with a Jeol JNM-4H-100 (100 MHz) spectrometer for solutions in $CDCl_3$ (internal Me_4Si). I.r. spectra were recorded with a Unicam SP-200 spectrophotometer.

trans-6-Acetyl-2-methoxy-5,6-dihydro-2*H*-pyran (**2**) was obtained by alkaline hydrolysis of ethyl 3-[6-(2-methoxy-5,6-dihydro-2*H*-pyran)]-3-oxopropionate[5].

trans-*6-Acetyl-2-methoxy-5,6-dihydro-2*H-*pyran oxime* (**3**). — Ketone **2** (41 g) was added to a solution of sodium acetate hydrate (60 g) and hydroxylamine hydrochloride (36.4 g) in water (160 ml). The mixture was shaken at room temperature for 5 h and then extracted with ether. The extract was washed with water, saturated aqueous sodium carbonate, and water, dried ($MgSO_4$), and concentrated. The residue was triturated with light petroleum to give **3** (36 g, 80%), m.p. 57–58° (from ethyl acetate–hexane); ν_{max}^{KBr} 3400, 1660, 1400, 1190, 1110, 1050, 960, 890, and 720 cm^{-1}. ^{1}H-N.m.r. data: δ 6.01 (m, 1 H, $J_{4,5}$ 10.5 Hz, H-4), 5.75 (m, 1 H, H-5), 4.90 (bs, 1 H, H-6), 4.44 (pd, 1 H, $J_{2,3pe}$ 4.0, $J_{2,3pa}$ 10.7 Hz, H-2), 3.45 (s, 3 H, OMe), 2.37 (m, 1 H, $J_{3pa,3pe}$ 14.5 Hz, H-3pa), 2.05 (m, 1 H, H-3pe), and 1.95 (s, 3 H, Me).

Anal. Calc. for $C_8H_{13}NO_3$: C, 56.1; H, 7.7; N, 8.2. Found: C, 56.0; H, 7.8; N, 7.9.

*Methyl 6-amino-2,3,4,6,7-pentadeoxy-*α-DL-erythro- (**4**) *and* -DL-threo-*hept-2-enopyranoside* (**5**). — A solution of **3** (36 g) in dry ether (500 ml) was added dropwise to a boiling suspension of lithium aluminium hydride (25 g) in ether (400 ml). After 5 h, reaction was complete (t.l.c.; chloroform–methanol, 95:5). The excess of reductant was decomposed with aqueous sodium hydroxide, and the precipitate was collected and washed thoroughly with ether. The combined ethereal solutions were dried and concentrated to dryness. The residue was distilled at 52–55°/0.4 Torr to give **4** + **5** (26.5 g, 80%), as a yellowish liquid; ν_{max}^{film} 3350, 1650, 1590, 1400, 1180, 1110, 1050, 970, 860, and 710 cm^{-1}. ^{1}H-N.m.r. data: δ 6.00 and 5.68 (2 m, 2 H, $J_{2,3}$ 10.5 Hz, H-2,3), 4.84 (bs, 1 H, H-1), 3.65 (m, 1 H, H-5), 3.44 (s, 3 H, OMe), 3.03 (m, 1 H, H-6), 2.03 (m, 2 H, H-4,4'), 1.64 (bs, 2 H, NH_2), and 1.14 (d, 3 H, Me-7).

Anal. Calc. for $C_8H_{15}NO_2$: C, 61.1; H, 9.6; N, 8.9. Found: C, 61.0; H, 9.6; N, 8.7.

*Methyl 6-acetamido-2,3,4,6,7-pentadeoxy-*α-DL-erythro- (**6**) and -β-DL-threo-*hept-2-enopyranoside* (**7**). — The mixture **4** + **5** (25 g) was acetylated with acetic anhydride (100 ml) in pyridine (50 ml). The mixture was concentrated to dryness

under diminished pressure and the residue was triturated with ether to give **6** (19.0 g), m.p. 97–99°. The mother liquor was concentrated to dryness and the residue was eluted from a column of silica gel with chloroform–methanol (99:1) to give, first, **7** (3.0 g, 9.1%), m.p. 119–121°, followed by **6** (4.0 g; total yield of **6**, 23 g, 70%).

Compound **6** had ν_{max}^{KBr} 3320, 1650, 1550, 1115, 1050, 990, 970, and 720 cm^{-1}. ^{1}H-N.m.r. data: δ 6.50 (bd, 1 H, $J_{6,NH}$ 8.3 Hz, NH), 5.97, 5.71 (2 m, 2 H, $J_{2,3}$ 10.5 Hz, H-2,3), 4.86 (bs, 1 H, H-1), 4.09 (m, 1 H, $J_{6,7}$ 6.5, $J_{5,6}$ 6.0 Hz, H-6), 3.77 (m, 1 H, $J_{5,4a}$ 9.0, $J_{5,4e}$ 5.4 Hz, H-5), 3.40 (s, 3 H, OMe), 2.00 (m, 5 H, H-4pa,4pe, AcO), and 1.21 (d, 3 H, Me-7).

Anal. Calc. for $C_{10}H_{17}NO_3$: C, 60.3; H, 8.6; N, 7.0. Found: C, 60.1, H, 8.6; N, 6.8.

Compound **7** had ν_{max}^{KBr} 3260, 1645, 1560, 1115, 1060, 1000, 970, 950, 900, 870, 760, and 720 cm^{-1}. ^{1}H-N.m.r. data: δ 6.15 (bd, 1 H, $J_{6,NH}$ 8.6 Hz, NH), 5.99,5.70 (2 m, 2 H, $J_{2,3}$ 10.5 Hz, H-2,3), 4.85 (bs, 1 H, H-1), 4.15 (m, 1 H, $J_{6,7}$ 7.0, $J_{5,6}$ 2.4 Hz, H-6), 3.84 (m, 1 H, $J_{5,4a}$ 10.0, $J_{5,4e}$ 4.3 Hz, H-5), 3.41 (s, 3 H, OMe), 2.00 (m, 5 H, H-4pe,4pa, AcO), and 1.28 (d, 3 H, Me-7).

Anal. Calc. for $C_{10}H_{17}NO_3$: C, 60.3; H, 8.6; N, 7.0. Found: C, 60.3; H, 8.6; N, 7.0.

Compounds **6** and **8** displayed lower R_F values than **7** and **9** in t.l.c. with chloroform–methanol (9:1) and benzene–ether–methanol (59:40:1).

*Methyl 6-acetamido-2,3-anhydro-4,6,7-trideoxy-α-*DL-manno- (**10**) *and* -allo-*hexopyranosides* (**11**). — A solution of **6** (1 g) and *m*-chloroperoxybenzoic acid (1.8 g) in chloroform (30 ml) was left at room temperature for 7 days, and then filtered and concentrated to dryness. The residue was crystallised from ethyl acetate and hexane to give **10** (0.38 g), m.p. 165–167°. The mother liquor was concentrated to dryness, and the residue was eluted from silica gel with ether to give, first, **10** (0.15 g; total yield, 0.53 g, 49%), followed by **11** (0.2 g, 18.5%), m.p. 136–139°.

Compound **10** had ν_{max}^{KBr} 3310, 1650, 1560, 1130, 1100, 1075, 1035, 990, 975, and 810 cm^{-1}. ^{1}H-N.m.r. data: δ 6.02 (bd, 1 H, $J_{6,NH}$ 7.5 Hz, NH), 4.95 (s, 1 H, H-1), 3.98 (m, 1 H, $J_{6,5}$ 4.9, $J_{6,7}$ 6.8 Hz, H-6), 3.75 (m, 1 H, H-5), 3.48 (s, 3 H, OMe), 3.40 (m, 1 H, H-3), 3.01 (d, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 2.00 (s, 3 H, AcO), 1.82–2.02 (m, 2 H, H-4pa,4pe), and 1.15 (d, 3 H, Me-7).

Anal. Calc. for $C_{10}H_{17}NO_4$: C, 55.8; H, 8.0; N, 6.5. Found: C, 55.6; H, 8.0; N, 6.1.

Compound **11** had ν_{max}^{KBr} 3360, 1670, 1545, 1295, 1200, 1160, 1130, 1070, 1050, 1030, 985, 865, and 830 cm^{-1}. ^{1}H-N.m.r. data: δ 6.17 (bd, 1 H, $J_{6,NH}$ 8.5 Hz, NH), 5.03 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1), 4.03 (m, 1 H, H-6), 3.33–3.80 (m, 3 H, H-2,3,5), 3.52 (s, 3 H, OMe), 1.59–2.23 (m, 2 H, H-4pa,4pe), 2.03 (s, 3 H, AcO), and 1.18 (d, 3 H, $J_{6,7}$ 6.8 Hz, Me-7).

Anal. Calc. for $C_{10}H_{17}NO_4$: C, 55.8; H, 8.0; N, 6.5. Found: C, 55.8; H, 8.0; N, 6.4.

*Methyl 6-acetamido-2,3-anhydro-4,6,7-trideoxy-β-*DL-gulo-*heptopyranoside* (**18**). — A solution of **7** (1.5 g) and *m*-chloroperoxybenzoic acid (2 g) in chloroform (50 ml)

was left at room temperature for 7 days, and then filtered and concentrated. The residue was crystallised from ethyl acetate and hexane to give **18** (1.2 g, 74%), m.p. 124–126°; ν_{max}^{KBr} 3250, 1640, 1560, 1110, 1085, 1060, 1030, 980, 870, and 810 cm^{-1}. ^{1}H-N.m.r. data: δ 6.14 (bd, 1 H, $J_{6,NH}$ 8.6 Hz, NH), 4.90 (s, 1 H, H-1), 4.01 (m, 1 H, $\sum J$ 31 Hz, H-6), 3.71 (m, 1 H, $\sum J$ 17.7 Hz, H-5), 3.46 (s, 3 H, OMe), 3.34 (m, 1 H, H-3), 2.97 (d, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 2.00 (s, 3 H, AcO), 1.86 (m, 2 H, H-4pa,4pe), and 1.20 (d, 3 H, $J_{6,7}$ 7.0 Hz, Me-7).

Anal. Calc. for $C_{10}H_{17}NO_4$: C, 55.8; H, 8.0; N, 6.5. Found: C, 55.9; H, 8.1; N, 6.6.

*Methyl 6-acetamido-3,4,6,7-tetradeoxy-α-*DL-arabino-*heptopyranoside* (**12**). — To a suspension of lithium aluminium hydride (4.3 g) in dry tetrahydrofuran (70 ml) was added dropwise a solution of **10** in the same solvent (30 ml). The mixture was stirred at room temperature for 6 h. The excess of the hydride was decomposed with water and aqueous 10% sodium hydroxide, and the ethereal solution was decanted, dried ($MgSO_4$), and concentrated to dryness. The residue was crystallised from ethyl acetate and hexane to give **12** (1.33 g), m.p. 123–125°. The mother liquor was concentrated, and the residue was eluted from silica gel with chloroform–methanol (98:2) to give more (0.5 g; total yield, 67%) of **11**; ν_{max}^{KBr} 3500, 3350, 1650, 1560, 1140, 1115, 1055, 1040, 1005, 980, 965, 840, and 730 cm^{-1}. ^{1}H-N.m.r. data: δ 6.10 (bd, 1 H, NH), 4.50 (s, 1 H, H-1), 3.96 (m, 1 H, H-6), 3.63 (m, 2 H, H-2,5), 3.33 (s, 3 H, OMe), 3.12 (bs, 1 H, OH), 1.94 (s, 3 H, AcO), 1.70–1.85 (m, 4 H, H-3,3′,4,4′), and 1.16 (d, 3 H, $J_{6,7}$ 6.9 Hz, Me-7).

Anal. Calc. for $C_{10}H_{19}NO_4$: C, 55.3; H, 8.8; N, 6.5. Found: C, 55.4, H, 9.0; N, 6.4.

*Methyl 6-acetamido-3,4,6,7-tetradeoxy-2-*O*-methanesulphonyl-α-*DL-arabino-*heptopyranoside* (**13**). — Treatment of **12** (54 mg) with methanesulphonyl chloride (27 mg) and pyridine (5 ml) at room temperature, in the usual way, gave **13** (60 mg, 81%), m.p. 101–103° (from ethyl acetate–hexane); ν_{max}^{KBr} 3430, 1650, 1530, 1350, 1170, 1115, 1050, 990, 950, 930, 890, 870, 810, and 750 cm^{-1}. ^{1}H-N.m.r. data: δ 5.86 (bd, 1 H, $J_{6,NH}$ 8.5 Hz, NH), 4.66 (s, 1 H, H-1), 4.47 (bs, 1 H, H-2), 3.96 (m, 1 H, H-6), 3.70 (m, 1 H, $J_{5,4e}$ 3.5, $J_{5,4a}$ 10.0 Hz, H-5), 3.31 (s, 3 H, OMe), 3.01 (s, 3 H, MsO), 1.98 (s, 3 H, AcO), 1.33–1.98 (m, 4 H, H-3a,3e,4a,4e), and 1.16 (d, 3 H, $J_{6,7}$ 6.5 Hz, Me-7).

Anal. Calc. for $C_{11}H_{21}NO_6S$: C, 44.7; H, 7.2; N, 4.7. Found: C, 44.5; H, 7.2; N, 4.7.

Heating of **13** (0.15 g) in methyl sulphoxide (6 ml) at 120° with sodium azide (0.25 g) for 48 h gave (after work-up) 80 mg of a substance that was identified as **6** (t.l.c., i.r., and ^{1}H-n.m.r. data).

*Methyl 6-acetamido-3,4,6,7-tetradeoxy-α-*DL-erythro-*heptopyranosid-2-ulose* (**14**). — A solution of **12** (100 mg) in benzene (2 ml) was oxidised with methyl sulphoxide (0.3 ml), pyridine (0.02 ml), trifluoroacetic acid (0.01 ml), and dicyclohexylcarbodi-imide (0.2 g). After 24 h, ether was added, the mixture was filtered, the filtrate was concentrated to dryness, and the residue was eluted from silica gel

to give **14** (85 mg, 85.8%) as a colourless syrup; ν_{max}^{film} 3350, 1735, 1650, 1550, 1100, 1040, 990, 950, 930, 900, 880, and 840 cm^{-1}. ^{1}H-N.m.r. data: δ 6.25 (bd, 1 H, $J_{6,NH}$ 8.0 Hz, NH), 4.51 (s, 1 H, H-1), 4.15 (m, 2 H, H-5,6), 3.44 (s, 3 H, OMe), 2.74 (dq, 1 H, $J_{3a,4e}$ 6.5, $J_{3a,4a}$ 12.5, $J_{4a,4e}$ 14.5 Hz, H-3a), 2.41 (m, 1 H, H-3e), 1.84–2.13 (m, 2 H, H-4a,4e), 2.01 (s, 3 H, AcO), and 1.20 (d, 3 H, $J_{6,7}$ 6.6 Hz, Me-7).

Ketone **14** (83.1%) was obtained from **12** on oxidation with ruthenium tetraoxide in carbon tetrachloride.

Heating of **14** (0.4 g) with pyridine (4 ml), methanol (4 ml), and hydroxylamine hydrochloride (0.4 g), with chromatography of the product, gave the oxime **15** (0.23 g, 53.7%), m.p. 138–139°; ν_{max}^{Nujol} 3340, 1620, 1560, 1455, 1100, 1080, 1030, 990, 970, 945, 920, 910, and 885 cm^{-1}. ^{1}H-N.m.r. data (pyridine): δ 5.21 (s, 1 H, H-1), 4.26 (m, 2 H, H-5,6), 3.59 (m, 2 H, OH, NH), 3.35 (s, 3 H, OMe), 1.59–2.45 (m, 4 H, H-3a,3e,4a,4e), 2.12 (s, 3 H, AcO), and 1.28 (d, 3 H, $J_{6,7}$ 6.0 Hz, Me-7).

Anal. Calc. for $C_{10}H_{18}N_2O_4$: C, 52.2; H, 7.9; N, 12.2. Found: C, 52.5; H, 7.8; N, 12.1.

*Methyl 2,6-diacetamido-2,3,4,6,7-pentadeoxy-α-*DL-ribo-*heptopyranoside* (**16**). — Oxime **15** (0.1 g) was reduced with a suspension of lithium aluminium hydride (0.1 g) in tetrahydrofuran (5 ml). After 3-h stirring at room temperature, the excess of the hydride was decomposed with ethyl acetate. The mixture was filtered and concentrated, and the residue was acetylated with acetic anhydride and pyridine. The product was eluted from silica gel to give **16** (30 mg, 26.7%), m.p. 229–231°; ν_{max}^{KBr} 3300, 1650, 1560, 1150, 1130, 1100, 1050, 1040, 990, 910, and 870 cm^{-1}. ^{1}H-N.m.r. data: δ 5.66 (m, 2 H, 2 NH), 4.60 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.04 (m, 2 H, H-2,6), 3.72 (m, 1 H, H-5), 3.36 (s, 3 H, OMe), 2.00 (s, 6 H, 2 AcO), 1.52–1.90 (m, 4 H, H-3a,3e, 4a,4e), and 1.15 (d, 3 H, $J_{6,7}$ 6.8 Hz, Me-7); lit.[4] $J_{1,2}$ 3.5 Hz.

Anal. Calc. for $C_{12}H_{22}N_2O_4$: C, 55.8; H, 8.6. Found: C, 55.1; H, 8.2.

Methyl 2,6-diacetamido-2,3,4,6,7-pentadeoxy-β-D-*ribo*-heptopyranoside (**19**, kindly furnished by Dr. P. J. L. Daniels) had m.p. 298–300°; ν_{max}^{KBr} 3300, 1650, 1565, 1150, 1130, 1070, 1040, 950, 875, and 835 cm^{-1}.

Mass spectra (abundances > 10%): **16** (17 eV): *m/e* 85 (20%), 112 (14), 113 (24), 114 (100), 126 (10), 139 (41), 140 (10), 155 (43), 172 (50), 198 (42), 199 (50), and 227 (11); **19** (15 eV): *m/e* 85 (15%), 87 (10), 112 (20), 113 (40), 114 (100), 121 (10), 126 (20), 139 (60), 140 (30), 155 (80), 156 (30), 167 (10), 172 (80), 198 (30), and 199 (70); **16** (70 eV): *m/e* 43 (83%), 44 (27), 55 (11), 56 (18), 57 (15), 60 (21), 69 (10), 70 (18), 71 (23), 72 (11), 85 (27), 86 (10), 96 (14), 97 (12), 98 (16), 112 (14), 113 (18), 114 (100), 126 (10), 130 (12), 139 (20), 155 (22), 172 (30), 198 (24), 199 (25), and 227 (7); **19** (70 eV): *m/e* 43 (97%), 44 (34), 55 (11), 56 (20), 57 (12), 60 (28), 69 (12), 70 (25), 71 (28), 72 (19), 84 (14), 85 (25), 86 (12), 96 (23), 97 (20), 98 (25), 112 (20), 113 (20), 114 (100), 126 (12), 130 (16), 139 (22), 140 (28), 155 (25), 156 (11), 172 (34), 198 (12), 199 (31), and 227 (1).

Samples (5 mg) of synthetic and natural methyl purpurosaminides B (**16** and **19**) were hydrolysed in 50% aqueous trifluoroacetic acid (reflux for 2 h). The reaction

mixtures were evaporated to dryness under diminished pressure; the i.r. spectra of both residues were identical.

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