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Note

Convenient syntheses of L-daunosamine and L-acosamine

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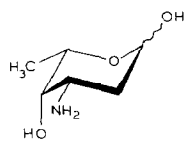
L-Daunosamine (**1**, 3-amino-2,3,6-trideoxy-L-*lyxo*-hexose) is the sugar component of the anthracycline antibiotics adriamycin[1], daunorubicin[1], and carminomycin[2], which, because of their activity against a wide range of experimental and human tumours[3], have attracted considerable attention. Adriamycin, in particular, possesses impressive activity against a wide range of solid tumours and has become established as a potent chemotherapeutic agent[4].

Studies on the mode of action of the anthracycline antibiotics and on structure–activity relationships have revealed the importance of the α-L-daunosaminyl residue in evincing biological activity[5]. Moreover, semi-synthetic analogues of adriamycin and daunorubicin in which, for example, L-daunosamine is replaced by L-acosamine (**2**, 3-amino-2,3,6-trideoxy-L-*arabino*-hexose) often display significant antitumour activity and/or lower toxicity than the parent anti-



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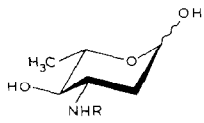
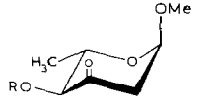
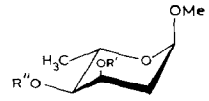


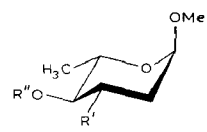
2 R = H
9 R = Ac



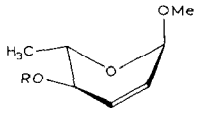
3 R = CH_2OMe



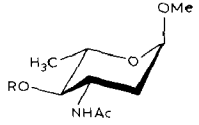
4 R′ = H, R″ = CH_2OMe
5 R′ = Ms, R″ = CH_2OMe



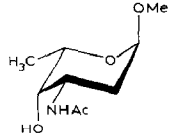
6 R′ = N_3, R″ = CH_2OMe
8 R′ = NHAc, R″ = CH_2OMe



7 R = CH_2OMe



10 R = H
11 R = Ac
12 R = Ms



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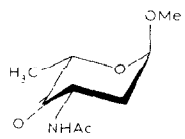
biotics[6]. The synthesis and proper evaluation of anthracycline analogues containing modified aglycon and/or sugar residues require easy access to relatively large amounts of L-daunosamine (**1**), L-acosamine (**2**), and structurally related sugars, a need that can often be met only by synthesis. Syntheses based on L-rhamnose and L-arabinose have furnished L-acosamine[7–9] (**2**) and L-daunosamine[9,10] (**1**), and the latter amino sugar has also been elaborated from D-mannose[11] and D-glucose[12]. Additionally, syntheses of derivatives of L-daunosamine[13,14] (**1**), L-acosamine[14,15] (**2**), and racemic **1**[16] have been developed from non-carbohydrate precursors.

Our interest in the synthesis of these important 3-amino-2,3,6-trideoxy-L-hexoses was evoked by the accessibility of methyl 2,6-dideoxy-4-*O*-methoxymethyl-α-L-*erythro*-hexopyranosid-3-ulose (**3**), which can be prepared in four steps from L-rhamnose[17]. The keto sugar **3** has already been transformed[17] into derivatives of L-ristosamine (3-amino-2,3,6-trideoxy-L-*ribo*-hexose*), and gave methyl 2,6-dideoxy-4-*O*-methoxymethyl-α-L-*ribo*-hexopyranoside (**4**), in excellent yield, on reduction with sodium borohydride. The mesylate **5** derived from **4** reacted with sodium azide in hot *N*,*N*-dimethylformamide to give the azide **6** (69% yield) and a small proportion of the unsaturated sugar **7** (identified by p.m.r. spectroscopy). Catalytic hydrogenolysis of **6** in the presence of acetic anhydride furnished **8**, which was smoothly transformed into *N*-acetyl-L-acosamine (**9**) on hydrolysis in boiling, aqueous acetic acid.

Removal of the methoxymethyl group from **8** with methanolic 1.5M hydrogen chloride at room temperature gave **10**[8], accompanied by a small proportion of the corresponding β-glycoside. For further characterisation, **10** was converted into the 4-acetate **11**[8]. In agreement with Richardson's findings[19], **10** could be transformed into methyl *N*-acetyl-α-L-daunosaminide (**13**), in roughly 50% overall yield, by way of an assisted solvolysis of the mesylate **12**. Standard reactions[10,11] can then be used to convert **13** into L-daunosamine hydrochloride (**1** · HCl).

In an attempt to improve the overall yield for the conversion of **10** into **13**, we examined the sequence **10** → **14** → **13**. Whereas **14** was reduced to **13** with high stereoselectivity and in 90% yield with L-Selectride[20], the oxidation of **10** to **14** proved to be much less efficient. Of various oxidants examined, the best results were obtained with pyridinium chlorochromate[21] and trifluoroacetic anhydride–methyl sulphoxide[22], which gave **14** in yields of 60 and 63%, respectively, leading



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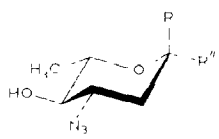
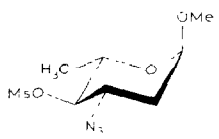


15 R′ = OMe, R″ = H
16 R = H, R″ = OMe



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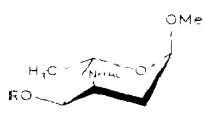

18 R = H
19 R = CH2OMe

*A daunorubicin analogue containing L-ristosamine in place of L-daunosamine displayed significant activity against experimental tumours[18].

to only a marginal improvement in the overall yield of **13** over that obtained by the original solvolytic procedure[19].

Alternatively, acid-catalysed methanolysis of **6** at room temperature afforded methyl 3-azido-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside[9,10] (**15**) and roughly 12% of the corresponding β-glycoside **16**. No difficulty was experienced in converting **15** in the mixture into the crystalline mesylate **17**, a known precursor[9,10] of L-daunosamine hydrochloride (**1** · HCl). Moreover, a straightforward procedure exists[8] for the conversion of **15*** into L-acosamine hydrochloride (**2** · HCl).

The foregoing procedures have been used to prepare several grammes of each of the hydrochlorides of L-daunosamine (**1**) and L-acosamine (**2**), and can be adapted to provide other synthetically useful derivatives of these amino sugars.

Although we have not quite achieved our goal of preparing all four 3-amino-2,3,6-trideoxy-L-hexoses from **3**, our procedures provide ready access to the *ribo*, *arabino*, and *lyxo* isomers. Our intended route to the L-*xylo* isomer was based on inversion of the configuration at C-4 of methyl 3-acetamido-2,3,6-trideoxy-α-L-*ribo*-hexopyranoside (**18**), which we hoped to obtain from **19** (readily prepared[17] from **3**). However, unlike the examples referred to above, acid-catalysed methanolysis of **19** gave an intractable mixture of products.

EXPERIMENTAL

General methods. — T.l.c. was performed on Kieselgel G, and detection was effected with 1% sulphuric acid. I.r. spectra were recorded for Nujol mulls or liquid films with a Perkin–Elmer Model 298 spectrometer, and p.m.r. spectra were recorded for solutions in deuteriochloroform with a Bruker Spectrospin (90 MHz) spectrometer, unless otherwise indicated. Optical rotations were measured with a Perkin–Elmer 141 automatic polarimeter, using 1-dm tubes. Melting points are uncorrected.

Methyl 2,6-dideoxy-3-O-methanesulphonyl-4-O-methoxymethyl-α-L-ribo-hexopyranoside (**5**). — To a cooled (0°) solution of **4** (2.17 g, 10.5 mmol; prepared as described[17] for the corresponding 4-*O*-methoxyethoxymethyl derivative) in anhydrous pyridine (22 mL) was added methanesulphonyl chloride (2.2 mL, 28.4 mmol), and the reaction mixture was kept overnight at room temperature and then poured into ice–water. After 15 min, the aqueous solution was extracted with chloroform, the extract was washed with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel (elution with 8:1 dichloromethane–acetone) gave **5** (2.56 g, 86%), $[\alpha]_D$ −190° (*c* 1.3, chloroform) (Found: C, 42.6; H, 7.3; S, 11.1. $C_{10}H_{20}O_7S$ calc.: C, 42.2; H, 7.1; S, 11.3%). P.m.r. data: δ 5.12 (q, 1 H, H-3), 4.73 (ABq, 2 H, J_{AB} 7 Hz, OCH_2O), 4.71 (d, 1

*The small proportion of **16** admixed with **15** is of no consequence, since it is also converted into **2** · HCl.

H, H-1), 4.10 (m, 1 H, H-5), 3.44, 3.36, and 3.09 (3 s, 9 H, 2 OMe and OMs), 2.38 (dd with fine splitting, 1 H, J_{gem} 15, $J_{2e,3}$ ~3 Hz, H-2*e*), 2.00 (dt, 1 H, $J_{1,2a} \approx J_{2a,3} \approx$ 4 Hz, H-2*a*), and 1.28 (d, 3 H, $J_{5,6}$ 7 Hz, Me-5).

With subsequent batches, the crude mesylate **5** was used in the next step without purification by chromatography.

*Methyl 3-azido-2,3,6-trideoxy-4-O-methoxymethyl-α-*L-arabino-*hexopyranoside* (**6**). — A solution of **5** (3.2 g, 11.3 mmol) in *N,N*-dimethylformamide (56 mL) containing sodium azide (5.6 g, 86 mmol) was heated overnight at 100°, cooled, filtered, and concentrated under reduced pressure. The residue was extracted with chloroform, and the extract was washed with a little water and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel (elution with 20:1 dichloromethane–acetone) gave, first, **6** (1.8 g, 69%), b.p. ~70° (bath)/0.5 mmHg, $[\alpha]_D$ −184° (*c* 1, chloroform); ν_{max} 2100 cm^{-1} (N_3) (Found: C, 46.8; H, 7.7; N, 18.1. $C_9H_{17}N_3O_4$ calc.: C, 46.7; H, 7.4; N, 18.2%). P.m.r. data: δ 4.80 (ABq, 2 H, J_{AB} 7 Hz, OCH_2O), 4.69 (d, 1 H, H-1), 3.91–3.53 (m, 2 H, H-3,5), 3.43 and 3.31 (2 s, 6 H, 2 OMe), 3.04 (t, 1 H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4), 2.16 (ddd, 1 H, J_{gem} 13, $J_{1,2e} \approx 1$, $J_{2e,3}$ 5 Hz, H-2*e*), 1.66 (ddd, 1 H, $J_{1,2a}$ 3.5, $J_{2a,3}$ 12 Hz, H-2*a*), and 1.29 (d, 3 H, $J_{5,6}$ 6 Hz, Me-5).

Continued elution afforded methyl 2,3,6-trideoxy-4-*O*-methoxymethyl-α-L-*erythro*-hex-2-enopyranoside (**7**; 92.5 mg, 4%*), b.p. ~110° (bath)/~15 mmHg, $[\alpha]_D$ −147° (*c* 0.8, chloroform) (Found: C, 57.4; H, 8.9. $C_9H_{16}O_4$ calc.: C, 57.4; H, 8.6%). P.m.r. data: δ 6.02 (d, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.73 (d with fine splitting, 1 H, H-3), 4.83 (s, 1 H, H-1), 4.73 (ABq, 2 H, J_{AB} 7 Hz, OCH_2O), ~3.82 (m, 2 H, H-4,5), 3.42 and 3.40 (2 s, 6 H, 2 OMe), and 1.30 (d, 3 H, $J_{5,6}$ 6 Hz, Me-5).

*Methyl 3-acetamido-2,3,6-trideoxy-4-O-methoxymethyl-α-*L-arabino-*hexopyranoside* (**8**). — A solution of **6** (0.183 g, 0.79 mmol) in methanol (20 mL) containing acetic anhydride (1 mL) and platinum(IV) oxide (0.2 g) was shaken overnight at room temperature under a slight overpressure of hydrogen. The catalyst and solvent were then removed, and toluene was added to, and evaporated from, the residue to remove the last traces of acetic anhydride. The residue was extracted with chloroform, and the extract was dried ($MgSO_4$) and concentrated under reduced pressure to give **8** (0.188 g, 96%), m.p. 134.5–136° (from ethyl acetate–hexane), $[\alpha]_D$ −21° (*c* 1, chloroform); ν_{max} 1650 and 1560 cm^{-1} (NHAc) (Found: C, 53.4; H, 8.6; N, 5.7. $C_{11}H_{21}NO_5$ calc.: C, 53.4; H, 8.6; N, 5.7%). P.m.r. data: δ 4.69 (ABq, 2 H, J_{AB} 6 Hz, OCH_2O), 4.67 (d, 1 H, H-1), 4.13 and 3.71 (m, 2 H, H-3,5), 3.39 and 3.31 (2 s, 6 H, 2 OMe), 3.07 (t, 1 H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4), 2.27 (dd, 1 H, J_{gem} 13, $J_{2e,3}$ 5 Hz, H-2*e*), 1.97 (s, 3 H, NAc), 1.61 (ddd, 1 H, $J_{1,2a}$ 3.5, $J_{2a,3}$ 12 Hz, H-2*a*), and 1.25 (d, 3 H, $J_{5,6}$ 6 Hz, Me-5).

*3-Acetamido-2,3,6-trideoxy-*L-arabino-*hexose (N-acetyl-*L-*acosamine)* (**9**). — A solution of **8** (0.207 g, 0.84 mmol) in water (5 mL) and acetic acid (2 mL) was boiled under reflux for 90 min, whereafter it was diluted with water (10 mL) and

*We suspect that losses of **7** occurred during concentration of the original reaction solution.

concentrated under reduced pressure with occasional additions of water. A solution of the residue in methanol was treated with charcoal, filtered, and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 7:3 ethyl acetate–methanol) gave **9** (0.14 g, 88%), m.p. 205–207° (after several recrystallisations from ethyl acetate containing a little methanol), $[\alpha]_D$ −21° (equil.; *c* 0.6, water); ν_{max} 1640 and 1560 cm^{-1} (NHAc) (Found: C, 50.8; H, 8.0; N, 7.1. $C_8H_{15}NO_4$ calc.: C, 50.8; H, 8.0; N, 7.4%). The p.m.r. spectrum of **9** in $(CD_3)_2SO$ was indistinguishable from that reported[23] for the D enantiomer having m.p. 199–201° (dec.), $[\alpha]_D$ +22° (equil.; *c* 1, water).

*Methyl 3-acetamido-2,3,6-trideoxy-α-*L-arabino-*hexopyranoside* (**10**). — A solution of **8** (0.647 g, 2.6 mmol) in methanolic hydrogen chloride (1.5M, 18 mL) was stirred at room temperature for 2 h, and then diluted with methanol, neutralised ($PbCO_3$), filtered, and concentrated under reduced pressure. The residue was extracted with warm ethyl acetate, and the extract was dried ($MgSO_4$) and concentrated under reduced pressure to give **10** (0.53 g, 99.7%), containing a small proportion of the β-glycoside, which was suitable for use in subsequent experiments. An analytical sample of **10** had m.p. 158–159.5° (from ethyl acetate–hexane) (Found: C, 53.4; H, 8.5; N, 6.9. $C_9H_{17}NO_4$ calc.: C, 53.2; H, 8.4; N, 6.9%), and its p.m.r. spectrum was indistinguishable from that reported[23] for the D enantiomer (m.p. 155–156°).

Acetylation of **10** with acetic anhydride in pyridine, in the usual way, gave methyl 3-acetamido-4-*O*-acetyl-2,3,6-trideoxy-*α*-L-*arabino*-hexopyranoside (**11**, 86%), m.p. 163–165° (from ethyl acetate–hexane), $[\alpha]_D$ −186° (*c* 1.2, methanol) {lit.[8] m.p. 163–164°, $[\alpha]_D$ −191° (*c* 0.52, methanol); D enantiomer[23] m.p. 161–162°, $[\alpha]_D$ +184° (*c* 0.9, methanol)}.

*Methyl 3-acetamido-2,3,6-trideoxy-α-*L-threo-*hexopyranosid-4-ulose* (**14**). — *(a) Using pyridinium chlorochromate*[21]. A solution of **10** (0.582 g, 2.9 mmol) in dichloromethane (6 mL) was added to a stirred solution of pyridinium chlorochromate (1.7 g, 7.9 mmol) in dichloromethane (13.5 mL) containing 3 Å molecular sieves[24] (1.34 g), and stirring was continued at room temperature for 3.5 h. The mixture was then dispersed, with stirring, in anhydrous ether (150 mL), and the ethereal solution was decanted from the spent oxidant and concentrated (after treatment with charcoal) under reduced pressure. Chromatography of the residue on silica gel (elution with 7:3 ethyl acetate–methanol) gave **14** (0.345 g, 60%), $[\alpha]_D$ −108 ±4° (*c* 0.8, chloroform); ν_{max} 1730 cm^{-1} (C=O), which eventually crystallised, but could not be recrystallised; a satisfactory elemental analysis could not be obtained for this compound, which contained (p.m.r. evidence) traces of impurities. P.m.r. data: δ 5.00 (m, 1 H, H-3), 4.85 (d, 1 H, H-1), 4.42 (q, 1 H, H-5), 3.46 (s, 3 H, OMe), 2.80 (dd with fine splitting, 1 H, J_{gem} 13, $J_{2e,3}$ 6 Hz, H-2*e*), 2.02 (s, 3 H, NAc), 1.91 (ddd, 1 H, $J_{1,2a}$ 3, $J_{2a,3}$ 12 Hz, H-2*a*), and 1.27 (3 H, d, $J_{5,6}$ 6 Hz, Me-5).

(b) Using trifluoroacetic anhydride–methyl sulphoxide[22]. To a stirred mixture of anhydrous methyl sulphoxide (1 g, 12.8 mmol) and dichloromethane (4 mL) at

−78° was added a solution of trifluoroacetic anhydride (1.68 g, 8 mmol) in dichloromethane (4 mL) followed, after 10 min, by a solution of **10** (0.544 g, 2.7 mmol) in dichloromethane (8 mL). Stirring was continued at −78° for 1 h, whereafter triethylamine (8 mL) was added and the solution was allowed to attain room temperature before dichloromethane (75 mL) was added. The organic solution was washed with a little water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue on silica gel (elution with 7:3 ethyl acetate–methanol) gave **14** (0.341 g, 63%) as a semi-crystalline solid, whose p.m.r. and i.r. spectra were essentially indistinguishable from those of the material obtained in (*a*).

Methyl 3-acetamido-2,3,6-trideoxy-α-L-lyxo-*hexopyranoside* (**13**). — A 100-mL three-necked flask equipped with a dropping funnel, a stirring bar, and a gas-inlet tube was flushed with nitrogen and charged with **14** (0.266 g, 1.32 mmol) in anhydrous tetrahydrofuran (23 mL). The contents of the flask were cooled to −40° before L-Selectride (~M; 3.5 mL, ~3.5 mmol) was added gradually so that the temperature was maintained at ~ −40°. Stirring was continued at −40° for 2 h, and the solution was then allowed to warm to −10° before 3M sodium hydroxide (1 mL) followed by aqueous 30% hydrogen peroxide (5 mL) were added, keeping the temperature below 15°. The solution was then saturated with potassium carbonate and diluted with chloroform, and the chloroform solution was decanted and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on silica gel (elution with 1:1 ethyl acetate–methanol) gave **13** (0.242 g, 90%), m.p. 183–185° (from ethyl acetate), $[\alpha]_D$ −236° (*c* 1, methanol). The i.r. and p.m.r. spectra of this material were indistinguishable from those {m.p. 183–185° (from ethyl acetate), $[\alpha]_D$ −234° (*c* 1.2, methanol)} of **13** prepared from **10**, in 51% yield, using Richardson's procedure[19] {lit. (D enantiomer) m.p. 183–185°, $[\alpha]_D$ +216° (*c* 1.15, methanol)[25]; m.p. 176–178°, $[\alpha]_D$ +222° (*c* 1.48, methanol)}[19].

Methyl 3-azido-2,3,6-trideoxy-4-O-methanesulphonyl-α-L-arabino-*hexopyranoside* (**17**). — A solution of **6** (0.18 g, 0.78 mmol) in methanolic 1.5M hydrogen chloride (5 mL) was stirred at room temperature for 30 min and then processed, as described for **10**, to give a mixture of **15**[9,10] and **16** (0.13 g, 89%), b.p. ~110° (bath)/0.8 mmHg, $[\alpha]_D$ −109° (*c* 1.1, chloroform). P.m.r. spectroscopy indicated that the mixture contained ≤12% of the β-glycoside **16**; otherwise, the p.m.r. spectrum was indistinguishable from that recorded for the α-glycoside **15** {lit.[9] b.p. 60–65° (bath)/0.05 mmHg, $[\alpha]_D$ −120° (*c* 1.3, chloroform)}

Methanesulphonylation[9] of the mixture of **15** and **16** furnished **17**, m.p. 90.5–91.5° (from ethyl acetate–hexane), $[\alpha]_D$ −123° (*c* 1.1, chloroform) {lit.[10] m.p. 89–90°, $[\alpha]_D$ −127° (chloroform)}, in 70% yield.

ACKNOWLEDGMENT

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