2,6-Diamino-2,3,4,6-tetradeoxy-D-*threo*-hexose ('D-epi-Purpurosamine')

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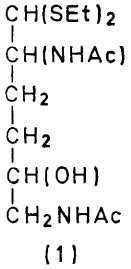
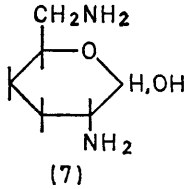
Summary Syntheses of derivatives of the title compound are described; consideration of their physical constants has shown that purpurosamine C (a component of gentamicin C_{1a}) is the D-*erythro*-isomer and has also assisted in the establishment of the structure of the related antibiotic, sisomicin.

ALTHOUGH the structure of gentamicin A has been established,[1] only the gross structure of the important broad spectrum antibiotic gentamicin C has been described.[2] The C complex[3] can be separated into gentamicins C_1, C_2 and C_{1a} that have each been shown[4] to be made up of three components, namely deoxystreptamine, a branched-chain



(1)

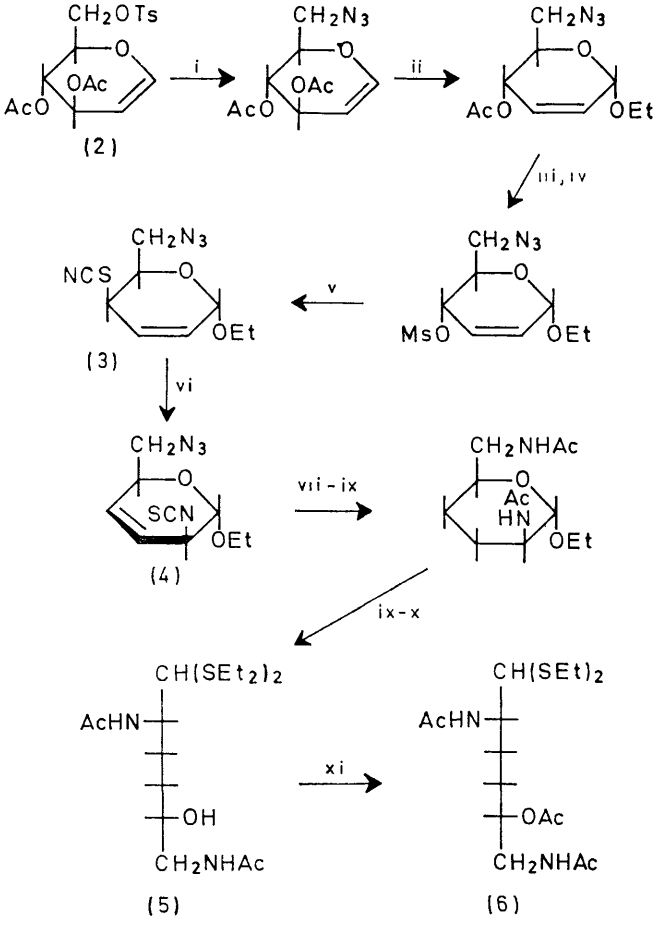


(7)

aminopentose garosamine,[5,6] and a hexose derivative, purpurosamine A, B, or C respectively. Thus it is only the third component that differentiates the three gentamicin C's. Mercaptolysis of penta-*N*-acetyl-gentamicin C_{1a} has led to the isolation of the diethyl dithioacetal of purpurosamine C, for which partial structure (**1**) has been reported.[4]

We now describe a synthesis of the D-*threo*-isomer (**5**) of (**1**), starting from the known[7] 3,4-di-*O*-acetyl-6-*O*-tosyl-D-glucal (**2**) (Scheme), which is essentially self-explanatory. The key step was the rearrangement of the allylic thiocyanate (**3**) to the isomeric isothiocyanate (**4**) in a similar manner to that described by Ferrier and Vethaviyasar[8] for the 6-*O*-mesyl analogue of (**3**).

The syrupy dithioacetal (**5**) had $[\alpha]_D$ −30° and its syrupy 5-*O*-acetyl derivative (**6**) had $[\alpha]_D$ −19° (in MeOH). These data must be compared with +27° for the crystalline purpurosamine C derivative (**1**) and +40° for its 5-acetate. Further, the n.m.r. spectra of the two series of compounds are different. Thus on this evidence alone, purpurosamine C must have the D- or L-*erythro* structures. However, Daniels[9] has shown by n.m.r. and $[\alpha]_D$ measurements on



SCHEME

Reagents: i, NaN_3, DMF; ii, EtOH, BF_3, Et_2O, C_6H_6; iii, NaOMe, MeOH; iv, MsCl, pyridine; v, KSCN, DMF; vi, heat, MeC_6H_5; vii, Ac_2O, AcOH; viii, H_2, Pt/C, EtOH; ix, Ac_2O, MeOH; x, EtSH, HCl; xi, Ac_2O, pyridine.

purpurosamine glycosides that, as expected by analogy with gentamicin A, they belong to the D-series. Thus purpurosamine C is 2,6-diamino-2,3,4,6-tetradeoxy-D-*erythro*-hexose (**7**) and the compounds synthesised by us are

derivatives of "D-*epi*-purpurosamine C". A synthesis of purpurosamine C is at present in progress.

The above data for (**5**) and (**6**) have also shown that they are the enantiomers of the 2,6-diacetamido-2,3,4,6-tetradeoxyhexose diethyl dithioacetal ($[\alpha]_D$ + 32°) and its 5-acetate ($[\alpha]_D$ + 21·6°) isolated[10] from degradation of the related antibiotic sisomicin,[11] and have thus enabled the complete structure of the diamino-sugar moiety of that substance to be established.

All new compounds gave satisfactory elemental analyses.

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