Structure of Prumycin, a 2,5-Diamino-2,5-dideoxypentose-containing Antibiotic

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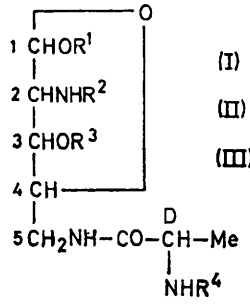
Summary The isolation of a new amino sugar, prumycin, the 5-D-alanyl derivative of 2,5-diamino-2,5-dideoxypentose, is described.

PRUMYCIN (I)[1] is a new antifungal antibiotic isolated from the fermentation of *Streptomyces sp.*, strain No. F.1028. It is a basic compound and forms a dihydrochloride

$C_8H_{17}N_3O_4,2HCl,H_2O$; m.p. 195 °C (decomp.); $[\alpha]_D^{25}$ (s 1·0, H_2O) +68·0° (3 min) → +155·2° (5 h); pK_a (H_2O) 7·02 and 8·16. (I) gave a positive colour reaction for a reducing sugar.



(I) R^1, R^2, R^3, R^4=H

(II) R^1, R^2, R^3, R^4=Ac

(III) R^1, R^3=H R^2, R^4=Ac

Acetylation of prumycin with acetic anhydride and pyridine afforded a tetra-acetate (II) $[\alpha]_D^{25}$ +33° (c 0·21, MeOH); M^+ *m/e* 387, $\nu_{C=O}$ (KBr) 1655, 1745 cm^{-1}. Hydrolysis of (II) with sodium methoxide in methanol gave a *NN'*-diacetyl prumycin (III) m.p. 180 °C (decomp.); $[\alpha]_D^{25}$ +52° (c 0·41, H_2O) $\nu_{C=O}$ (KBr) 1650 cm^{-1}.

Acid hydrolysis of prumycin with 6N-HCl at 100 °C for 4 h gave a ninhydrin positive substance which was identified as D-alanine by t.l.c., n.m.r., and o.r.d.[2] $[\alpha]_{300}$ −39°, $[\alpha]_{217}$ −810°, $[\alpha]_{207}$ 0°, and $[\alpha]_{205}$ +360° (c 0·03, 95% EtOH). That the carboxyl group of the alanine group was joined to (I) *via* an amide linkage was established from the i.r. spectrum (KBr) of prumycin dihydrochloride [1675 cm^{-1} ($\nu_{C=O}$) and 1555 cm^{-1} (amide II)].

Prumycin gave a positive Elson–Morgan reaction[3] but a negative Morgan–Elson colour reaction[4] behaving as 2-amino-2-deoxy-D-glucose in these tests. In contrast, (III) responded to the Morgan–Elson test, just as does 2-acetamido-2-deoxy-D-glucose, but with higher colour intensity (154%). From studies carried out by Jeanloz and Trémège[5] and by Kuhn and co-workers[6] which demonstrated that the colour reaction occurs with 2-acetamido-2-deoxy-aldose only if the 4-hydroxyl and aldehyde groups are free, it was concluded that the sugar fraction of diacetyl prumycin is a diaminopentose with an aldehyde grouping at position 1, acetylamino group at 2 and a free hydroxyl at 4.

On periodate oxidation[7,8] prumycin consumed 3·0 mol of oxidant in the course of 6 h indicating that the D-alanyl group is attached to an amino group on C-5.

The data presented are consistent with structure (I). It is worth noting that up to the present, 2,5-diaminopentoses were unknown. The inability to isolate it from acid hydrolysis of prumycin indicates that 2,5-diaminopentose is unstable, as are the 5-amino sugars.[9]

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