SYNTHESIS OF TUNICAMINYL URACIL

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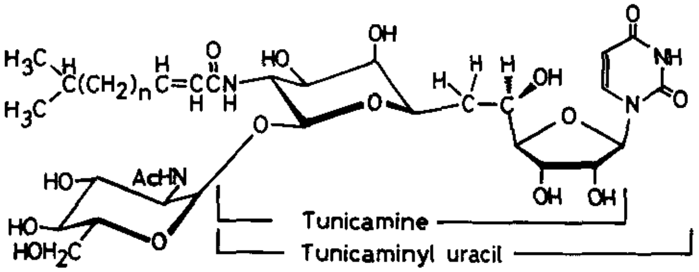
A moiety of antibiotic tunicamycins consisting of uracil and tunicamine[1)] has been designated tunicaminyl uracil which is a key intermediate for a total synthesis of tunicamycins. Now we wish to report the successful synthesis of tunicaminyl uracil derivative.



Tunicamycins (n=8,9,10,11)

A KF catalyzed addition[2)] of 3-O-acetyl-5-deoxy-1,2-O-isopropylidene-5-nitro-α-D-ribofuranose to methyl 2-(benzyloxycarbonyl)amino-2-deoxy-3,4-O-isopropylidene-α-D-galactodialdopyranoside-(1,5) gave a C_{11}-dialdose derivative in 51% yield. Dehydration of the product, followed by oxidation, hydrogenation and acetylation afforded the tunicamine derivative, mp 186-187°C; $[\alpha]_D^{18}$+197° (c 0.3, $CHCl_3$). Condensation of the derivative with bis(trimethylsilyl)uracil in the presence of $SnCl_4$ gave a product in 55% yield. Catalytic hydrogenolysis of the product, followed by acetylation afforded the tunicaminyl uracil derivative: 1-[methyl 10'acetamido-2',3',5',8',9'-penta-O-acetyl-1',6',10'-trideoxy-α-L-galacto-D-allo-undecodialdo-(11'S)-pyranoside-(11',7')-furanosyl-(1,4)]-uracil in 63% yield, mp 124-127°C; $[\alpha]_D^{18}$+84.3° (c 0.7, $CHCl_3$), which was identical with an authentic sample.

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