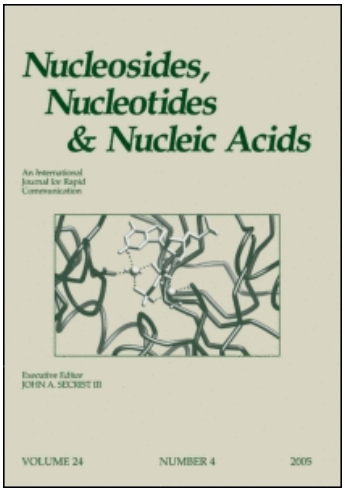

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Synthesis of *O*-β-D-Ribofuranosyl-(1''-2')-adenosine-5''-*O*-phosphate

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SYNTHESIS OF *O*-β-D-RIBOFURANOSYL-(1″- 2′)-ADENOSINE-5″-*O*-PHOSPHATE

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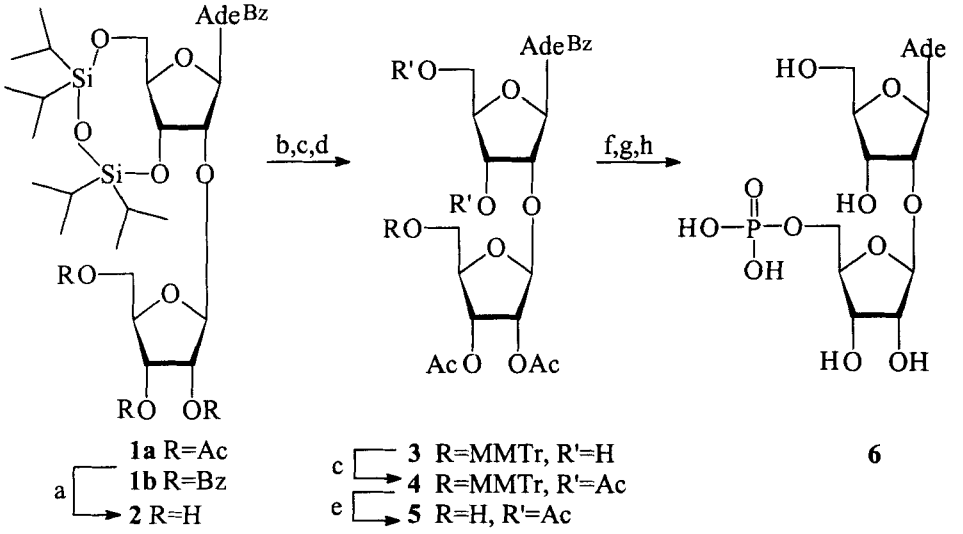
ABSTRACT: The first synthesis of *O*-β-D-ribofuranosyl-(1″-2′)-adenosine-5″-*O*-phosphate starting from protected 2′-*O*-β-D-ribofuranosyladenosine has been performed.

Recently a minor nucleoside was isolated from yeast methionine initiator tRNA and its structure was determined as *O*-β-D-ribofuranosyl-(1″-2′)-adenosine-5″-*O*-phosphate (**6**)[1,2]. Here we report on the first synthesis of this compound starting from **1**. The synthesis was performed according to the following scheme.



a. 0.1 M NaOMe; b. MMTrCl/Py; c. Ac_2O/Py; d. Bu_4NF/THF; e. *p*-TsOH/ $CHCl_3$/MeOH; f. $NC(CH_2)_2OPO_3H_2$/DCC/Py; g.NH_3/MeOH; h. 1M NaOH.

Fully protected 2'-*O*-β-D-ribofuranosyladenosines (**1**) were prepared by condensation of N^6,3',5'-*O*-protected adenosine with slight excess of 1,2,3,5-tetra-*O*-acetyl(benzoyl)-β-D-ribofuranoses in the presence of 1.2 eq. of tin tetrachloride in dichloroethane (0°C, under nitrogen)[3,4]. It should be mentioned that the yield of disaccharide with *O*-benzoyl groups was higher (50% and 75% for **1a** and **1b** respectively).

Treatment of **1a** with NaOMe for 10 min gave **2** in 82 % yield. The same deprotection of **1b** proceeded much more slowly and was accompanied by the formation of several products. The overall yields for these two steps using *O*-acetyl and *O*-benzoyl groups were near the same (41-42%). The 5'-hydroxyl group of additional *O*-ribofuranosyl moiety in **2** was protected with monomethoxytrityl group. The conversion of **2** → **5** was achieved using standard methods without difficulties. The phosphorylation of **5** with subsequent deprotection gave **6**[5] in overall good yield. The structures of **1-6** were proven by NMR spectroscopy.

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5. ^{1}H NMR (400.13 MHz) (D_2O) of **6**: 8.33 s (1H, H-8), 8.17 s (1H, H-2), 6.17 d (1H, $J_{1',2'}$ = 6.3 Hz, H-1' Ado), 4.97 d (1H, $J_{1',2'}$ = 1.0 Hz, H-1' Rib), 4.82 dd (1H, $J_{2',3'}$ = 5.3 Hz, H-2' Ado), 4.56 dd (1H, $J_{3',4'}$ = 3.2 Hz, H-3' Ado) 4.25 ddd (1H, $J_{4',5'a}$ = 2.5 Hz, $J_{4',5'b}$ = 3.6 Hz, H-4' Ado), 4.16 dd (1H, $J_{3',2'}$ = 4.7 Hz, $J_{3',4'}$ = 6.5 Hz, H-3' Rib), 4.13 dd (1H, H-2' Rib), 3.92 ddd (1H, $J_{4',5'a}$ = 4.2 Hz, $J_{4',5'b}$ = 6.3 Hz, H-4' Rib), 3.89 dd (1H, $J_{5'a,5'b}$ = - 12.9 Hz, H-5'a Ado), 3.80 dd (1H, H-5'b Ado), 3.68 ddd (1H, $J_{5'a,5'b}$ = -11.6 Hz, $J_{5'a,P}$ = 6.1 Hz, H-5'a Rib), 3.44 ddd (1H, $J_{5'b,P}$ = 6.4 Hz, H-5'b Rib). ^{31}P NMR (161.98 MHz) (D_2O): 1.92.