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First, Solid Support-Aided Introduction of Isopentyladenosine, Hypermodified Nucleoside of tRNA, into Oligoribonucleotide Chain

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FIRST, SOLID SUPPORT-AIDED INTRODUCTION
OF ISOPENTYLADENOSINE, HYPERMODIFIED NUCLEOSIDE OF tRNA,
INTO OLIGORIBONUCLEOTIDE CHAIN.

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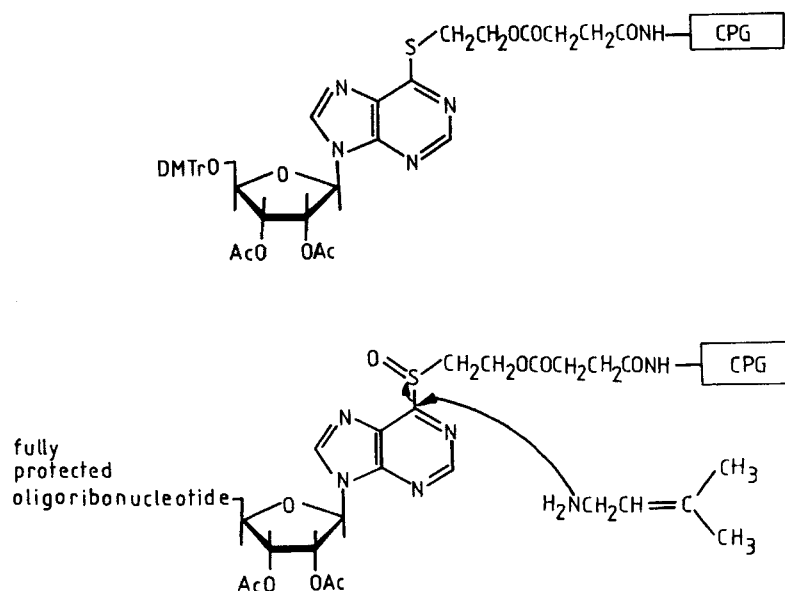
Abstract: A concept of chemical, solid support-aided, introduction of N(6)-isopentenyladenosine, into oligoribonucleotide chain is outlined.

Hypermodified nucleosides of tRNA have been subjected to numerous chemical and structural studies /1/. Synthesis of oligoribonucleotides containing these multifunctional molecules presents considerable challenge. Since our pioneering work /2/ on the synthesis of tRNA anticodon loop heptamer composing of N(6)-threonylcarbonyladenosine, only one case, concerning introduction of various hypermodified wobble-uridines to short oligoribonucleotides, was fully investigated /3,4/. Phosphotriester chemistry, in solution, was applied in both above cases.

Here, we would like to present a new concept (compare /5/) of N(6)-isopentenyladenosine introduction into oligoribonucleotide chain reflecting recent developments in general chemical RNA synthesis. Multi-step synthesis of the model AA*A*i(6)A consists of the following key reactions:

1. transformation of inosine into N(5'-O-DMT-2',3'-O-di-O-acetylnebularin-6-yl)pyridinium chloride /6/,
2. its quantitative reaction with mercaptoethanol to form 6(2-hydroxyethyl)tiopurine analogue /7/,
3. 2-hydroxyethyl function esterification with succinic anhydride and subsequent active ester formation followed by coupling with LCAA-CPG

4. 5'-O-DMT removal and solid supported extention of RNA chain with application of 5'-O-DMT-2'-O-TBDMSi-N-benzoyladenosine-3'-O-(N,N-diisopropyl)(2-cyanoethyl)phosphoramidites; final trityl on,
5. oxidation with buffered (pH 6.5) bromine to form 6-alkylsulphoxide linkage,
6. S_NAr-displacement with isopentenylamine resulting in hypermodification and detachment of partially protected AAAi(6)A from the support,
7. final deprotection, purification and analysis of AAAi(6)A.



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