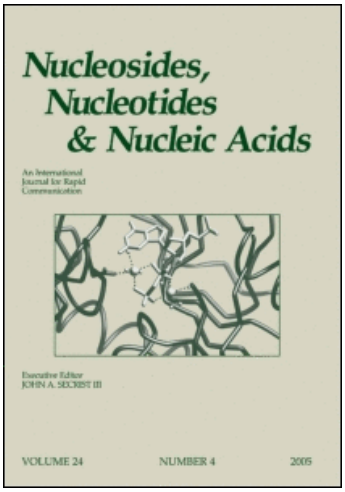

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Selective Deuteration Labelling of 2'-Deoxyguanosine at the Carbon C-4' Position

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SELECTIVE DEUTERATION LABELLING OF 2'-DEOXYGUANOSINE AT THE CARBON C-4' POSITION

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Selective incorporation of deuterium within the sugar moiety of nucleosides and oligonucleotides can be used for different purposes including isotopic effect determination in mechanistic studies, mass spectrometry fragmentation investigations, nuclear magnetic resonance analyses. We wish to report a simple method which allows the selective deuteration labelling of 2'-deoxyguanosine at the C-4'position through the intermediary of 9-(2-deoxy-ß-D-erythropento-1,5-dialdo-1,4-furanosyl)guanine. Heating of aqueous pyridine solution [1:1] of 2'-deoxyguanosine-5'-aldehyde for 1 hr at 60°C leads to a partial epimerisation of carbon C-4' with subsequent formation of 9-(2-deoxy-α-L-threopento-1,5-dialdo-1,4-furanosyl)guanine in 40% yield. A likely intermediate of this reaction appears to be a 5'-enol derivative. Similar treatment of 2'-deoxyguanosine-5'-aldehyde in D_2O-pyridine [1-1] gives after $NaBH_4$ reduction 60% of 2'-deoxyguanosine which is selectively deuterated at the C-4' position. The extend of the isotopic labelling was up to 95% as determined by high resolution electron impact mass spectrometry and ^1H NMR analyses. Heating of the aqueous pyridine solution of 2'-deoxyguanosine-5'-aldehyde for a longer period (3-4 hrs) gave rise to two other nucleosides which where assigned as 9-(2-deoxy-ß-D-threo-pentofuranosyl)guanine and 9-(2-deoxy-α-L-erythro-pentofuranosyl)guanine. A retro-aldol mechanism appears to be involved in the epimerization reaction which takes place at carbon C-3'.

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