SUPPORTING INFORMATION

Enzymatic Synthesis of 2'-Deoxyribonucleosides of 8-Azapurines and 8-Aza-7-deazapurines

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1. TABLE

<table>
<thead>
<tr>
<th>Compound a)</th>
<th>Yield b) (%)</th>
<th>UV spectrum c)</th>
<th>$^{13}$C NMR (δ$_{TMS}$, ppm) d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{max}$ nm</td>
<td>$\lambda_{min}$ nm</td>
<td>C2</td>
</tr>
<tr>
<td>8-Aza-2'-deoxyadenosine (15)(^{1,3})</td>
<td>66</td>
<td>217, 278</td>
<td>234</td>
</tr>
<tr>
<td>8-Aza-2'-deoxyguanosine (16)(^{2,3})</td>
<td>60</td>
<td>215, 254</td>
<td>231</td>
</tr>
<tr>
<td>8-Aza-7-deaza-2'-deoxyadenosine (17)(^{4}a)</td>
<td>77</td>
<td>219, 259</td>
<td>273</td>
</tr>
<tr>
<td>8-Aza-7-deaza-2'-deoxy-8'-methylguanosine (18)(^{4})</td>
<td>76</td>
<td>224, 251</td>
<td>274</td>
</tr>
<tr>
<td>8-Aza-7-deaza-2'-deoxyinosine (19)(^{4,10})</td>
<td>68</td>
<td>219, 251</td>
<td>274</td>
</tr>
<tr>
<td>2-amino-8-aza-6-chloro-7-deaza-9-(2-deoxy-β-D-ribofuranosyl)purine (20)(^{10})</td>
<td>25</td>
<td>235</td>
<td>305</td>
</tr>
</tbody>
</table>

a) Purine numbering is used throughout.
b) Yields are given for pure isolated products.
c) The UV spectra were measured in water (pH 7.0), except for 8-aza-2'-deoxyadenosine (in EtOH).
d) The NMR spectra were obtained from Bruker Avance-500-DRX (Bruker, Germany) using DMSO-d$_6$ as a solvent; *) means tentative assignment.

References
7 Seela, F.; Steker, H. Heterocycles 1985, 23, 2521.
Synthesis of 2-amino-8-aza-6-chloro-7-deaza-9-(2-deoxy-β-D-ribofuranosyl)purine (20).

HPLC of the raw product after work-up of the reaction mixture.

UV spectrum of peak at the $R_t = 6.65$ min.

UV spectrum of peak at the $R_t = 8.42$ min.

UV spectrum of peak at the $R_t = 9.15$ min.

Mass-spectrum of peak at the $R_t = 6.65$ min.
Mass-spectrum of peak at the $R_t = 8.42$ min.

Mass-spectrum of peak at the $R_t = 9.15$ min.
2. The progress of the synthesis 2-deoxy-β-D-ribonucleosides of 8-aza- and 8-aza-7-deazapurines (one-pot synthesis).

**Standard reaction conditions**: total volume 2 mL; 2 mM ATP, 50 mM KCl, 3 mM MnCl₂, 20 mM Tris-HCl (pH 7.5); 1.3 mM 2-deoxy-D-ribose, 1 mM heterocyclic base; units of enzymes: RK¹⁵ (9), PPM¹⁶ (4) and PNP¹⁴ (14); 40 °C; yields by HPLC of nucleoside (%) and time of the reaction (h): 1⁵ (8; 15), 1⁶ (23; 25), 1⁷ (52; 25), 1⁸ (50; 20) and 1⁹ (60; 10).

The formation of 8-azaadenosine (1⁵) (◊) and 8-azaguanosine (1⁶) (□).

The formation of nucleosides 8-aza-7-deazapurine nucleosides (1⁷) (◊), (1⁸) (□) and (1⁹) (△).