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Nucleosides, Nucleotides and Nucleic Acids

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Synthesis Of Pyrrolo[2,3-b]Pyridine Nucleosides by Solid-Liquid Phase-Transfer Glycosylation and Deoxycenation of 4-Chloropyrrolo[2,3-d]Pyrimidine 2'-Deoxyribofuranosides

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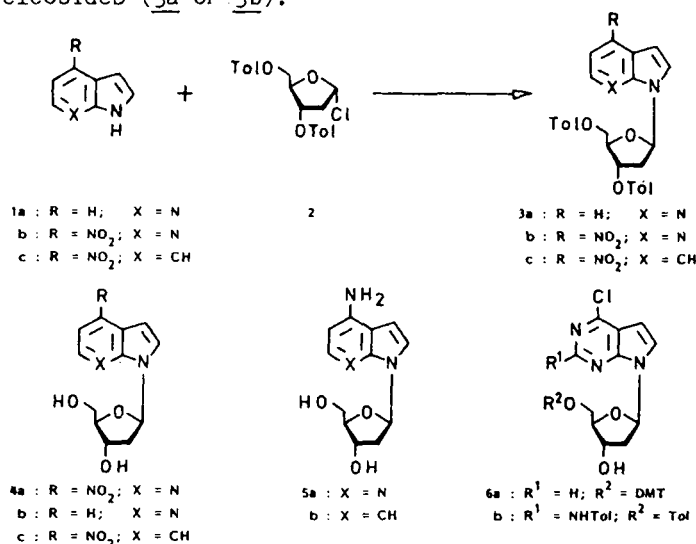
SYNTHESIS OF PYRROLO[2,3-b]PYRIDINE NUCLEOSIDES BY SOLID-LIQUID PHASE-TRANSFER GLYCOSYLATION AND DEOXYGENATION OF 4-CHLOROPYRROLO[2,3-d]PYRIMIDINE 2'-DEOXYRIBOFURANOSIDES

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Abstract.- Pyrrolo[2,3-b]pyridine 2'-deoxynucleosides were synthesized stereoselectively by solid-liquid phase-transfer glycosylation. Also 4-chloropyrrolo[2,3-d]pyrimidine 2'-deoxyribofuranosides were deoxygenated yielding a series of new base-modified 2',3'-dideoxynucleosides.

Glycosylation of the pyrrolo[2,3-b]pyridines 1a or 1b with the deoxy-halogenose 2 employing solid-liquid phase-transfer conditions (powdered KOH, 0.1 mol-% TDA-1, MeCN) [1] yielded stereoselectively the protected 2'-deoxynucleosides (3a or 3b).

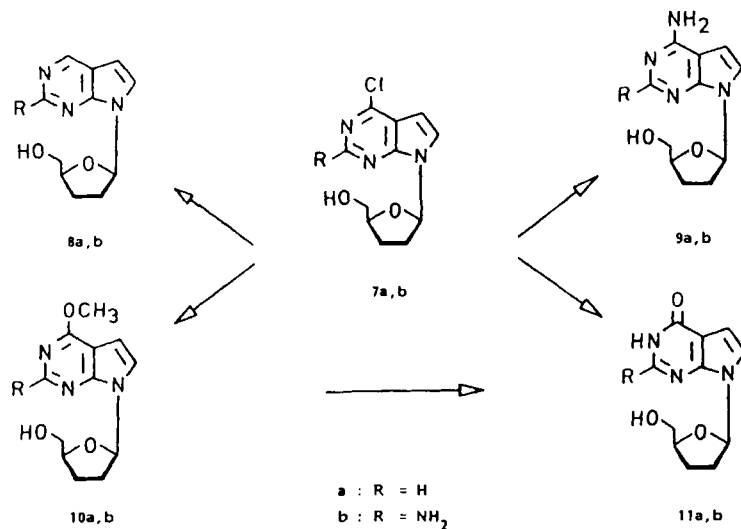


Deprotection of 3a or 3b gave 4a and 4b, respectively. Catalytic hydrogenation of 4a afforded 5a. Under the same conditions the indole nucleoside 5b was synthesized. Earlier, its 4-deamino derivative has been prepared stereoselectively via its anion [2]. Recently, the 4-amino derivative 5b was also obtained employing NaH as condensation reagent [3].

Tab. ^{13}C NMR Data of Pyrrolo[3,2-b]pyridine and Indole Nucleosides in DMSO

Compnd	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a
3a	126.1	101.5	120.9	129.0	116.8	142.7		147.5
3b	132.0	100.9	113.3	145.2	110.8	143.3		150.6
3c	130.4	102.6	122.5	139.5	118.5 ^a	121.2	118.0 ^a	137.9
4a	132.1	100.4	113.0	145.0	110.4	143.0		150.5
4b	126.4	100.8	120.8	128.9	116.4	142.4		147.2
4c	130.8	102.0	122.4	139.4	118.3 ^a	121.0	117.7 ^a	137.8
5a	122.0	98.6	108.4	148.6	100.2	143.4		148.1
5b ^a	122.9	102.7	122.0	141.6	100.4	117.2	98.5	137.1
	C-1'	C-2'	C-3'	C-4'	C-5'	C=O	CH ₃	
3a	81.0	36.0	75.3	83.2	64.4	165.4/165.6	21.2	
3b	81.4	36.2	75.1	83.7	64.2	165.4/165.6	21.2/21.3	
3c	81.4	36.6	74.8	85.3	64.2	165.5/165.6	21.2/21.3	
4a	83.3	DMSO	71.0	87.6	61.9			
4b	83.0	DMSO	71.2	87.2	62.2			
4c	85.0	DMSO	70.7	87.5	61.7	^a tentative		
5a	84.4	DMSO	71.5	87.4	62.5			
5b	84.4	DMSO	70.9	86.8	62.1			

Apart from the synthesis of 2'-deoxynucleosides we have obtained 2', 3'-dideoxynucleosides containing the pyrrolo[2,3-d]pyrimidine moiety. As common starting materials the 4-chloro compounds **6a** and **6b** were used to give the **7a** or **7b** by deoxygenation. The latter were converted into a series of new 2', 3'-dideoxynucleosides (**8-11**, formula scheme) [4].



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