ANOMALOUS NUCLEOSIDES AND RELATED COMPOUNDS

XII. Synthesis of Some Nitrophenylhydrazine Derivatives of Periodate-Oxidized Nucleosides*

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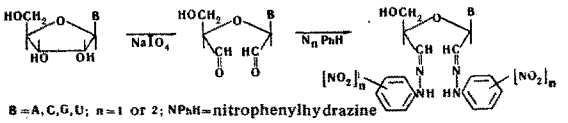
The synthesis of some nitrophenylhydrazones of products obtained by the oxidation of nucleosides with sodium periodate has been effected.

In the study of the structure of nucleic acids and, in particular, the stability of their terminal glycosidic bond by the periodate oxidation method, various derivatives of the nucleosides are used [1-3]. We have performed the synthesis of some nitrophenylhydrazones of products obtained by the oxidation of nucleosides with sodium periodate in the following way:



B = A, C, G, U; n = 1 or 2; NPhH = nitrophenylhydrazine

Table 1

Compound	Mp, °C	N, % found	N, % calculated	Empirical formula	ε × 10⁻⁴ at 260 nm	Yield, %
o-NPHAR*	164—167	28,53	28,77	$C_{22}H_{21}N_{11}O_6$	2,57	52
m-NPHAR	154—158	28,55	28,77	$C_{22}H_{21}N_{11}O_6$	3,30	45
p-NPHAR	193—198	28,13	28,77	$C_{22}H_{21}N_{11}O_6$	2,33	50
p-NPHUR	147—152	21,97	21,87	$C_{21}H_{20}N_8O_8$	1,75	37
2,4-DNPHAR	192—195	30,10	29,11	$C_{22}H_{19}N_{13}O_{10}$	3,15	51
2,4-DNPHGR	167—170	28,28	28,39	$C_{22}H_{19}N_{13}O_{11}$	2,73	40
2,4-DNPHCR	183—185	25,51	25,62	$C_{21}H_{19}N_{11}O_{11}$	2,23	62
2,4-DNPHUR	165—167	23,24	23,25	$C_{21}H_{18}N_{10}O_{12}$	2,60	40

*A) adenine; G) guanine; C) cytosine; U) uracil; R) riboside; NPH) nitrophenylhydrazine; D) di.

After oxidation for 20 min, a solution of 0.8 mM of a nucleoside in 10 ml of 0.1 M sodium periodate solution was passed through a column (10 ml) of Dowex-1 in the acetate form. The column was eluted with 100 ml of 0.02 M acetic acid. The eluate was collected in a vessel containing 2 g of sodium acetate, and then 1.5 mM of the appropriate phenylhydrazine in a mixture of 50 ml of ethyl acetate and 75 ml of ethanol was added. The solution was left overnight at room temperature and was then evaporated in a vacuum of 12 mm at a bath temperature of 30°C. The product that deposited was freed from contamination with nitrophenylhydrazine by washing in aqueous ethanolic solution with ethyl acetate. The condensation products, yellow or orange substances, were readily soluble in the lower alcohols and were fairly unstable, especially in the presence of moisture. Some characteristics of the nitrophenylhydrazine derivatives synthesized are given in Table 1.

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*For part XI, see [4].