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Mikhail K. Gratchev; Edward E. Nifant'ev

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New Chiral Phosphocontaining Heterocycles on the Basis of Natural Oligohydroxyl Compounds

MIKHAIL K. GRATCHEV and EDWARD E. NIFANTYEV

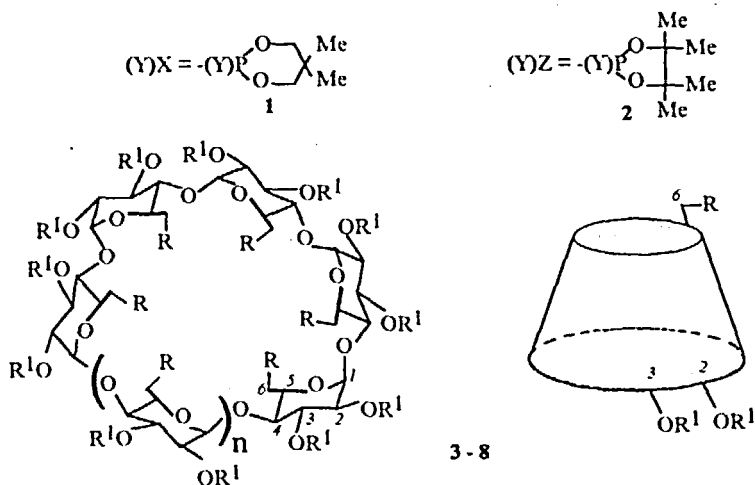
*Moscow Pedagogical State University, Chemistry Department, Nesvizski per. 3,
Moscow 119021, Russia*

Principal possibilities of creation of chiral phosphocontaining heterocycles on the basis of natural derivatives of cyclodextrins and dianhydro-D-mannitol are discussed. The obtained compounds possess an internal chiral cavity of a definite size and represent an interest for the solution of modern tasks of biomimetic and supramolecular chemistry.

Keywords: cyclodextrins; phosphorylation

Cyclodextrins (α -, β -, γ -c.ds.: $n=1,2,3$; $R=OH$, $R^1=H$) are available natural cyclic oligosaccharides having high potentiality for the fine organic synthesis. Recently we have studied the synthesis of perphosphorylated c.ds. using chlorophosphites 1,2 [1]. At present we report the phosphorylation of per-6-bromo-per-6-deoxy- β -c.d. 3. We aimed to yield water-soluble, phosphocontaining c.ds. having polar heads which would permit c.d. cavity to be orientated by a definite manner at the phase boundary "organic liquid - water". It is known that c.ds. exhibit low water- and organosolubility therefore restricting their practical application.

At first, we studied the alkylation of pyridine by bromoderivative 3 ($n=2$) with the formation of the corresponding per-6-pyridinium salts of per-6-deoxy- β -c.d. 4. Product 4 turned out to be readily soluble in polar solvents (DMFA, CH_3OH) and, noteworthy, - in water. By combining the methods of pyridine alkylation and phosphorylation [1], we obtained 2,3-perthionophosphates 6-per-6-deoxypyridinium salts of β -c.d. 5, which contain polar ionic heads on the smaller rim of c.d. frame and show good solubility in pyridine, DMFA and limited solubility in CH_3OH . Then from c.ds. derivatives 3 and 4 other c.ds. derivatives (6-8) having hydrophilic polar heads on one of the c.d. rims may be easily obtained by standard phosphorylation methods.



- 1: $\text{Cl}-(\text{Y})\text{X}$, $\text{Y} = \text{l.e.p.}$; 2: $\text{Cl}-(\text{Y})\text{Z}$, $\text{Y} = \text{l.e.p.}$; 3: $\text{R} = \text{Br}$, $\text{R}^1 = \text{H}$;
 4: $\text{R} = \text{HN}^+\text{C}_5\text{H}_5\text{Br}^-$, $\text{R}^1 = \text{H}$; 5: $\text{R} = \text{HN}^+\text{C}_5\text{H}_5\text{Br}^-$; $\text{R}^1 = (\text{Y})\text{X}$, $\text{Y} = \text{S}$;
 6: $\text{R} = \text{Br}$; $\text{R}^1 = (\text{Y})\text{X}$, $\text{Y} = \text{S}$; 7: $\text{R} = \text{Br}$, $\text{R}^1 = (\text{Y})\text{Z}$, $\text{Y} = \text{S}$;
 8: $\text{R} = \text{Br}$; $\text{R}^1 = (\text{Y})\text{X}$, $\text{Y} = \text{O}$;

We paid special attention to the obtaining of *interglucoside* 2,3'-cyclophosphorylated c.ds. Known structural peculiarities of c.ds. gave evidences in favour of just *interglucoside* 2,3'-cyclophosphorylation. Such structures should be promising macromolecules with rigid frame combining volume chiral cavities in the form of "bowls" and highly reactive P(III)-N bonds ($\text{X} = \text{l.e.p.}$) which might be easily functionalized using various methods of P(III)-N chemistry for the solution of some tasks of supramolecular and biomimetic chemistry. Per-2,3'-cyclophosphorylated c.ds. were obtained by interaction of c.ds. per-6-silyl derivatives of c.ds. with tri- and diamidophosphites.

