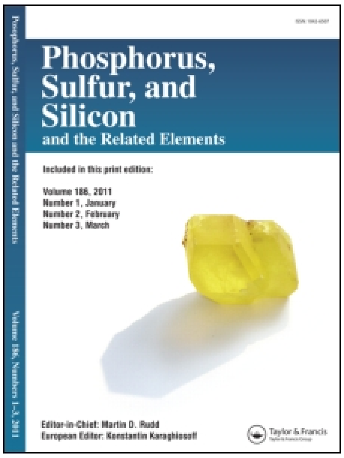

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New Chiral Phosphocontaining Heterocycles on the Basis of Natural Oligohydroxyl Compounds

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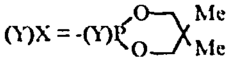
Principal possibilities of creation of chiral phosphocontaining heterocycles on the basis of natural derivatives of cyclodextrins and dianhydro-D-mannitol are discussed. The obtained compounds possess an internal chiral cavity of a definite size and represent an interest for the solution of modern tasks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



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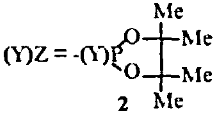

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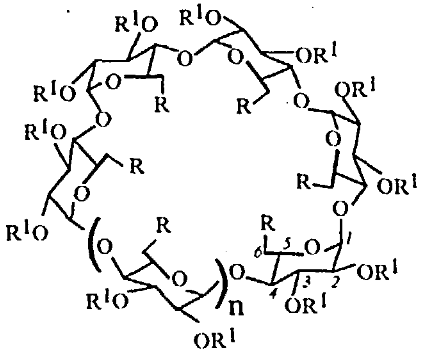
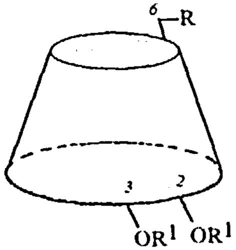




3 - 8

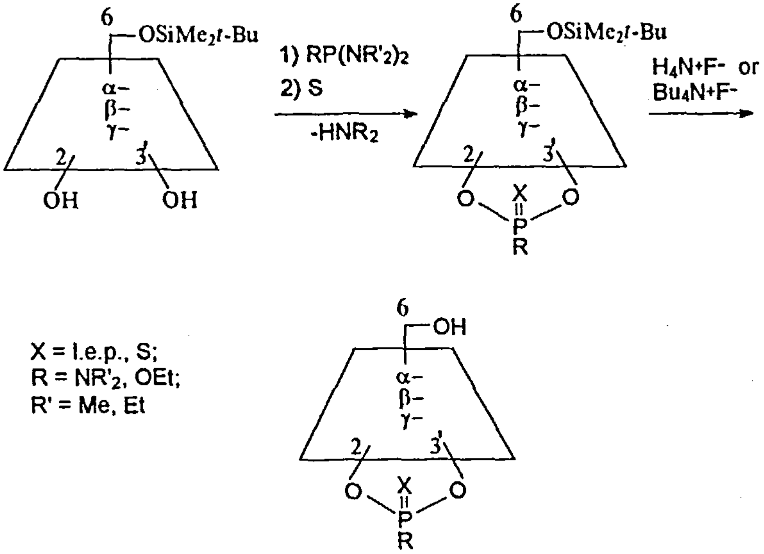
1: Cl-(Y)X, Y = l.e.p.; **2**: Cl-(Y)Z, Y = l.e.p.; **3**: R = Br, R^1 = H;

4: R = $HN^+C_5H_5Br^-$, R^1 = H; **5**: R = $HN^+C_5H_5Br^-$; R^1 = (Y)X, Y = S;

6: R = Br; R^1 = (Y)X, Y = S; **7**: R = Br, R^1 = (Y)Z, Y = S;

8: R = Br; R^1 = (Y)X, Y = O;

We paid special attention to the obtaining of *inter*glucoside 2,3'-cyclophosphorylated c.ds. Known structural peculiarities of c.ds. gave evidences in favour of just *inter*glucoside 2,3'-cyclophosphorylation. Such structures should be promising macromolecules with rigid frame combaining volume chiral cavities in the form of "bowls" and highly reactive P(III)-N bonds (X=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.



X = l.e.p., S;
R = NR'_2, OEt;
R' = Me, Et