

LETTERS
TO THE EDITOR

Phosphorylation of Chitosan
with Hexamethylphosphorous Triamide

I. Yu. Kudryavtsev and E. E. Nifant'ev

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia
e-mail: zaq@ineos.ac.ru

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Chitosan and its phosphorus-containing derivatives, chitosan phosphate in particular, can be used as biocompatible materials [1], sorbents for uranium extraction [2], membranes [3, 4], and chiral matrices for metal complex catalysts [5]. At the same time, phosphorous acid derivatives of chitosan have not been described. In view of the versatile reactivity of trivalent phosphorus derivatives, they are perspective starting materials for obtaining various new materials.

In this work we explored the possibility for preparing phosphorous amidoesters derived from chitosan by phosphorylation of the latter with hexamethylphosphorous triamide. This reagent was earlier used for phosphorylation of various hydroxy compounds, including sugars [6]. It was found that the reaction under usual conditions [refluxing a mixture chitosan and $(\text{Me}_2\text{N})_3\text{P}$ in anhydrous acetonitrile in the presence of dimethylamine hydrochloride (20 mol % per polymer chain unit)] resulted in a low phosphorylation degree: The resulting material contain about 0.5% of phosphorus. One conceivable reason for such a low substitution degree is the highly dense packing of chitosan macromolecules, formed by an extended intermolecular H-bond network, which restricts diffusion of the phosphorylating reagent. We attempted to destroy this network by introducing a loosening agent forming competitive H bonds with hydroxy and amino groups of the polysaccharide. For such an agent we used $\text{Me}_2\text{NH}_2\text{Cl}$ (2 mol per polymer chain unit). This allowed the phosphorus content to be increased to 2.5%, which corresponds to the substitution degree of 20%.

Thus, the developed approach opens up new possibilities for synthesis of phosphorous amidoesters on the chitosan matrix.

Phosphorylation of chitosan with hexamethylphosphorous triamide. A mixture of 0.322 g (2 mmol per polymer chain unit) of a powdered and dried chitosan (SK-1000), 0.652 g of $(\text{Me}_2\text{N})_3\text{P}$, 0.033 g of $\text{Me}_2\text{NH}_2\text{Cl}$, and 5 ml of anhydrous acetonitrile was refluxed for 36 h with stirring with a magnetic stirrer under a dry nitrogen atmosphere. The precipitate that formed was filtered off, washed with acetonitrile (5×5 ml) and ether (5×5 ml), and dried in a vacuum. Yield 0.32 g, light brown powder, insoluble in ordinary organic solvents. Found, %: N 8.82; P 0.51.

Similarly, from 0.652 g of $(\text{Me}_2\text{N})_3\text{P}$ and 0.326 g of $\text{Me}_2\text{NH}_2\text{Cl}$ we prepared 0.38 g of chitosan phosphorous amidoester. Found, %: N 8.84; P 2.52.

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