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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### Bio-Relevant Derivatives of Calixarene Phosphonic Acids

S. Cherenok<sup>a</sup>; A. Vovk<sup>b</sup>; I. Muravyova<sup>b</sup>; A. Marcinowicz<sup>c</sup>; J. Poznanski<sup>c</sup>; O. Muzychka<sup>b</sup>; V. Kukhar<sup>b</sup>; W. Zielenkiewicz<sup>c</sup>; V. Kalchenko<sup>a</sup>

<sup>a</sup> Institute of Organic Chemistry, NAS of Ukraine, Kyiv, Ukraine <sup>b</sup> Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine, Kyiv, Ukraine <sup>c</sup> Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

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## Bio-Relevant Derivatives of Calixarene Phosphonic Acids

S. Cherenok,<sup>1</sup> A. Vovk,<sup>2</sup> I. Muravyova,<sup>2</sup> A. Marcinowicz,<sup>3</sup>  
J. Poznanski,<sup>3</sup> O. Muzychka,<sup>2</sup> V. Kukhar,<sup>2</sup>  
W. Zielenkiewicz,<sup>3</sup> and V. Kalchenko<sup>1</sup>

<sup>1</sup>Institute of Organic Chemistry, NAS of Ukraine, Kyiv Ukraine

<sup>2</sup>Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine, Kyiv, Ukraine

<sup>3</sup>Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

*The calix[4]arenes functionalized at the macrocyclic upper rim with  $\alpha$ -hydroxyphosphonic,  $\alpha$ -aminophosphonic or methylenebisphosphonic acid groups were synthesized. The complexes formed between the bio-relevant calix[4]arene derivatives and amino acids or dipeptides as well as inhibition effects of calix[4]arene phosphonic acids on alkyl phosphatases activity were studied.*

**Keywords** Calixarene; phosphonic acids; enzyme; inhibition; amino acids

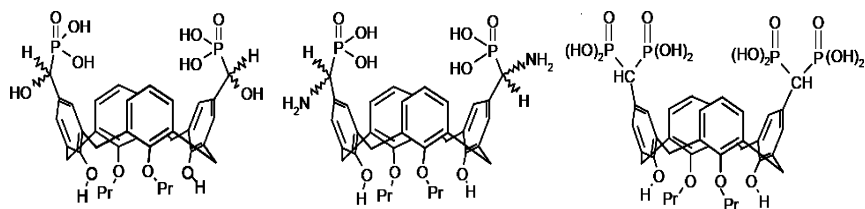
Calixarenes endowed with amino acid or peptide units demonstrate a high bioactivity.<sup>1</sup> Within the project, we have synthesized and investigated a series of the cone-shaped calix[4]arenes functionalized at the macrocyclic upper rim with biorelevant  $\alpha$ -hydroxyphosphonic or  $\alpha$ -aminophosphonic or methylenebisphosphonic acid groups.<sup>2–4</sup>

Complexation of calix[4]arene bis- $\alpha$ -hydroxyphosphonic acids (*Racemic* or *Meso* forms) with a series of natural amino acids and dipeptides was investigated by calorimetry, NMR and molecular modelling methods.<sup>3</sup> The association constants of the host-guest complexes in methanol (up to 45000 M<sup>-1</sup>) were determined. Hydrophobic, electrostatic, N-H- $\pi$ , C-H- $\pi$  interactions in the host-guest complexes are discussed.

Calix[4]arenes grafted with the  $\alpha$ -hydroxyphosphonic or  $\alpha$ -aminophosphonic or methylene-bis-phosphonic acid groups significantly overcome modelling acyclic phosphonic acids in inhibition of

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Address correspondence to V. I. Kalchenko, Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kyiv 94 02094 Ukraine. E-mail: vik@bpci.kiev.au



bovine intestinal and porcine kidney alkaline phosphatases.<sup>2,4</sup> In Tris-HCl buffer (pH 9) the (*R,R*) diastereomer of calixarene bis- $\alpha$ -aminophosphonic acid demonstrates 50 fold higher potency than the (*S,S*) diastereomer.<sup>4</sup>

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