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LETTERS TO THE EDITOR

Membrane Transport of Organic Acids by *N*-Methylphosphorylated Amino Acids

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Earlier we have shown that the three-component Kabachnik-Fields reaction can be successfully applied to prepare mono- and bis- N-methylphosphorylated derivatives of amino acids [1, 2]. In particular, starting from glycine, β-, and (*S*)-α-alanine we prepared 2-[*N*,*N*-bis(dioctylphosphorylmethyl)amino]acetic **I**, 2-[(*S*)-*N*,*N*-bis(dioctylphosphorylmethyl)amino]propionic **II**, 2-[(*S*)-*N*-dioctylphosphorylmethylamino]propionic **III**, and 3-[*N*,*N*-bis(dioctylphosphorylmethyl)amino] propionic **IV** acids with high yields.

Herein we report on the membrane transport properties of that products towards transfer of oxalic, glycolic, glutaric, malic, tartaric, and citric acids in the course of the extraction through lipophilic liquid supported membranes under the conditions listed elsewhere [3]. The membranes were prepared via impregnation of porous VLADiSART FMPTFE-0.2 Teflon filters (pores 0.2 μm, thickness 50 μm) with 0.1 mol/L solution of the tested carrier in dodecane under reduced pressure (20 mmHg). As follows from the tabulated data, the highest transfer rate for all the tested carriers was found in the cases of oxalic and glutaric acids, the other acids were transported with noticeably lower efficiency. In a separate measurement, we demonstrated that the passive diffusion of the studied acidic substrates through the membrane was practically absent (the flow being of $<10^{-7}$ mol min^{-1} m^{-2} without any carrier); hence, the trans-membrane flow was totally dependent on the stability and lipophilicity of the hydrogen-bonded complexes formed by the carrier and the substrate in the membrane phase. Evidently, the decreased transport rate in the case of hydroxycarboxylic acids as compared to the carboxylic acids is due to the presence of excessive hydroxyl groups leading to an increase hydrophilicity of the formed H-complexes.

Comparison of the transport with bis- (**II**) and monophosphorylated (**III**) α-alanine derivatives revealed the higher efficiency in the former case. The observed difference could be due to the fact that the transported complex should be formed via the both phosphoryl groups of compound **II**; that was unlikely due to the

Transfer flow ($\times 10^6$), mol min^{-1} m^{-2} of the tested organic acids with compounds **I**–**IV** as carriers

Carrier	Oxalic acid	Glycolic acid	Glutaric acid	(*S*)-Malic acid	(*R*,*R*)-Tartaric acid	Citric acid
I	418.4±8.1	77.3±1.8	287.2±11.3	41.2.±2.3	8.9±0.5	72.6±2.6
II	321.1±8.9	69.5±0.6	228.1±13.2	33.5±3.4	5.2±0.7	69.4±1.9
III	227.3±6.8	48.6±0.9	172.4±8.2	18.7±1.8	2.4±0.5	4.6±0.6
IV	510.4±21.2	34.3±1.1	1870.5±37.9	53.7±1.8	13.5±0.9	57.3±3.4

steric reasons. On the other hand, decreased transportation efficiency in the case of monophosphine oxide **III** could be explained by formation of the intramolecular hydrogen bond between the phosphoryl and the secondary amine groups; that complicates the formation of the transport complex with the acid substrates. Similar effect was observed earlier in the cases of other aminophosphorylated liquid-phase and membrane extractants [3].

Compound **IV** revealed the highest rate of glutaric acid transport; that was likely due to the β-positioning of the amino group with respect to the carboxyl one. Seemingly, such mutual location of the groups favored the interaction between the carrier and the substrate. However, well-reasoned conclusion on the relationship between the structures of the involved compounds and the efficiency of transmembrane carriage requires more detailed study of the process and will be reported separately.

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