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Biocatalyzed kinetic resolution of racemic mixtures of chiral α-aminophosphonic acids

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ABSTRACT

Several fungal species namely: *Aspergillus niger*, *Aspergillus parasiticus*, *Penicillium funiculosum*, *Trigonopsis variabilis* and two different strains of *Fusarium oxysporum* were tested toward racemic mixtures of following phosphonic acids: 1-amino-2-methylpropanephosphonic acid, 1-aminophenylmethanephosphonic acid and 1-amino-2-phenylethanephosphonic acid. Application of *F. oxysporum* strain (UW1) allowed obtaining optically pure *S*-isomer of 1-aminophenylmethanephosphonic acid and *R*-isomer of 1-amino-2-phenylethanephosphonic acid, whereas biotransformation of racemic mixture of 1-amino-2-methylpropanephosphonic acid with *F. oxysporum* strain (DSM 12646) cells resulted in obtaining pure enantiomer of *R*-configuration.

1. Introduction

Diversified biological activity of aminophosphonic acids and their derivatives causes, that they have found a wide range of application [1–10]. First compound of this class, 1-aminomethanephosphonic acid, was synthesized by Pikl during the Second World War, in 1943, but more extensive studies, which shown their noteworthy properties arising from structural analogy between α-aminophosphonic acids and natural amino acids, were undertaken notably later [11]. These compounds are valuable for medicine, because of their mammalian toxicity, which has been reported to be negligible. Phosphonopeptide alafosfalin (Fig. 1) shows broad antibacterial activity against both Gram-positive and Gram-negative microorganisms. Similar to β-lactam antibiotics, alafosfalin inhibits the biosynthesis of bacterial cell walls, but the mechanism of its action is different. Specific dipeptide permeases transport this molecule into the cells. There, by means of intracellular hydrolysis, alanine and α-aminoethanephosphonic acid, which is the inhibitor of alanine racemase involved in the biosynthesis of peptidoglycan, are produced. What is important, also some strains resistant to commonly used antibacterial agents, such as kanamycin, gentamicin or tetracycline, are susceptible to alafosfalin [12].

It should be emphasized, that only the (*S*,*R*) diastereoisomer of alafosfalin shows significant antibacterial activity [13]. It is not surprising, because in the most cases, compounds exerting biological activity are chiral molecules with defined absolute configuration. It must be considered especially during design and preparation of new drugs. That is why the efficient methods of synthesis of the optically pure aminophosphonates are being intensively investigated.

Simultaneously, in recent years scientist are focused on application of environmentally-friendly technologies. Dynamic development of green chemistry is observed and biocatalysis is becoming a standard technology for the production of chemicals on an industrial scale [14–17]. However biocatalytic methods leading to optically pure aminophosphonic products are rather rare, so it was an inspiration for presented work. Undertaken efforts allowed developing a simple, economic and efficient method of resolution of racemic mixtures of α-aminophosphonic acids and as a result, desired enantiomers were obtained as pure enantiomers or meaningly enriched racemic mixtures.

2. Experimental

2.1. General: substrates synthesis and characterization

All chemicals were commercially available. Substrates for biotransformation were synthesized according to standard procedure described in literature [18,19] and (if necessary) purified by column chromatography (Dowex 50WX8, 200–400 mesh) or by recrystallization from ethyl alcohol:water mixture (3:1, v/v).

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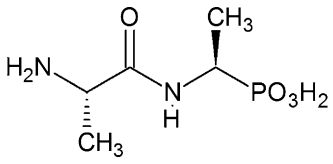

Fig. 1. Alafosfalin.

2.1.1. 1-Amino-2-methylpropanephosphonic acid (Val^P)

^{31}P NMR δ (ppm): 13.44.

^{1}H NMR δ (ppm): 0.95 (dd, J = 6.9 Hz, 6H, $(CH_3)_2CH$), 2.00–2.15 (m, 1H, $(CH_3)_2CH$), 2.94 (dd, J = 6.3 Hz, 1H, CHP).

2.1.2. 1-Aminophenylmethanephosphonic acid (Phg^P)

^{31}P NMR δ (ppm): 10.60.

^{1}H NMR δ (ppm): 4.19 (d, J = 15.5 Hz, 1H, CHP), 7.29 (s, 5H, Ph).

2.1.3. 1-Amino-2-phenylethanephosphonic acid (Phe^P)

^{31}P NMR δ (ppm): 11.51.

^{1}H NMR δ (ppm): 2.58–2.77 (m, 1H, CHP), 3.34–3.80 (m, 2H, CH_2), 7.14–7.36 (m, 5H, Ph).

The ^{1}H and ^{31}P NMR spectra were recorded on Bruker Avance™ 600 spectrometer or Bruker Avance DRX 300 spectrometer at 298 K. The optical rotation was measured using the polarimeter PolAAr 31.

2.2. Fungal strains

Fusarium oxysporum (DSM 12646) and *Trigonopsis variabilis* (DSM 70714) were purchased from DSMZ, Germany. *Aspergillus niger* (OP1) was a kind gift from the Opole University, Poland. *F. oxysporum* (UW1) was a kind gift from the University of Wroclaw, Poland. *Aspergillus parasiticus* (NRRLY 2999) was a kind gift from the Anadolu University, Turkey. *Penicillium funiculosum* (Thom S3) was isolated from soil sample and identified by Klimek-Ochab [20].

2.3. Cultivation of microorganisms

All cultures were grown in 250-mL flasks containing 100 mL of appropriate medium on a rotary shaker (130 rpm) at room temperature for 3 days, until the mid-log growth phase was reached.

P. funiculosum (Thom S3) and *A. parasiticus* (NRRLY 2999) were cultivated on commercially available Potato Dextrose Broth.

A. niger (OP1) was cultivated on special medium for optimal D-amino acid oxidase production, this medium was consisted of: 4 g/L casamino acids, 1 g/L KH_2PO_4, 0.1 g/L $MgSO_4{\bullet}7H_2O$, 0.5 g/L yeast extract, 10 g/L glycerol (as an effective carbon source for enzyme production) and enzyme synthesis inducer (D-valine or D-phenylalanine) in final concentration of 30 mM [21].

T. variabilis (DSM 70714) was cultivated on Universal Medium For Yeasts, which was consisted of 3 g/L yeast extract, 3 g/L malt extract, 5 g/L peptone from soybeans and 10 g/L glucose.

F. oxysporum (UW1) was cultivated on three different media: (a) Czapek-Dox Medium, which was consisted of 30 g/L sucrose, 0.5 g/L $MgSO_4{\bullet}7H_2O$, 0.5 g/L KCl, 2.64 g/L $(NH_4)_2SO_4$, 0.01 g/L $FeSO_4$ and 0.5 g/L KH_2PO_4 [22]; (b) special medium containing inducer: 18 g/L glucose, 4 g/L K_2HPO_4, 4 g $(NH_4)_2SO_4$, 4 g/L yeast extract, 1 g/L $MgSO_4{\bullet}7H_2O$, 0.5 g/L $CaCl_2{\bullet}2H_2O$, 0.1 g/L H_3BO_3, 0.04 g/L $NaMoO_4$, 0.04 g/L $ZnSO_4{\bullet}7H_2O$, 0.045 g/L $CuSO_4{\bullet}7H_2O$, 0.025 g/L $FeSO_4{\bullet}7H_2O$ and inducer (D-valine or D-phenylalanine) in final concentration of 15 mM [23]; (c) commercially available Potato Dextrose Broth.

F. oxysporum (DSM 12646) was cultivated on Malt Extract Peptone Broth containing 30 g/L malt extract and 3 g/L soya peptone.

Table 1
Data for the NMR samples preparation.

α-Aminophosphonic acid (abbreviation)	The amount of sample	The amount of α-cyclodextrin	pH value
Val^P	27 mg	39 mg	10
Phg^P	20 mg	58 mg	2
Phe^P	20 mg	58 mg	10

After 3 days of cultivation, biomass was separated by filtration (*P. funiculosum*, *A. parasiticus* and *A. niger*) or centrifugation (*T. variabilis*: 4500 rpm/15 min; *F. oxysporum*: 6000 rpm/15 min). Then the pellet was washed with distilled water and centrifuged again and the cells were applied for particular biotransformation procedure.

2.4. Biotransformation procedures

(I) *P. funiculosum*. Wet fungal biomass (10 g) was transferred into 100-mL flask containing 50 mL of inducer solution (D-Val, L-Val, D-Phe or L-Phe, respectively) in final concentration of 30 mM. Induction was carried out for 3 days in room temperature with shaking at 130 rpm. Then the biomass was separated by filtration, washed with distilled water and added to 100-mL flask containing 50 mL of aqueous solution of substrate (Val^P in case of cells induced with valine; for cells induced with phenylalanine Phg^P or Phe^P were applied) in final concentration of 5 mM. The reaction mixtures were incubated on a rotary shaker (130 rpm) at room temperature for 4 days.

(II) *A. niger*. Wet fungal biomass (10 g) was used as biocatalyst or preincubated for 24 h under starvation conditions (in 50 mL of distilled water at 130 rpm and room temperature). Biotransformation was carried out according to procedure above (I) with the addition of 0.5 g of glycerol. Biotransformation was carried out at 130 rpm and at room temperature for 3 days.

(III) *A. parasiticus*, *T. variabilis* and *F. oxysporum*. Wet fungal biomass (10 g) was used directly after cultivation as biocatalyst or was preincubated for 24 h under starvation conditions (in 50 mL of distilled water at 130 rpm and room temperature). Biotransformation was carried out for 3 days as described above (I).

Subsequently, after bioconversion was completed, biocatalyst was removed by filtration (*P. funiculosum*, *A. parasiticus* and *A. niger*) or centrifugation (*T. variabilis*: 4500 rpm/15 min and *F. oxysporum*: 6000 rpm/15 min) and the filtrate/supernatant was evaporated.

2.5. Enantiomeric excess assignment

The enantiomeric excess was determined by means of ^{31}P NMR spectroscopy with the addition of α-cyclodextrin as a chiral discrimination agent [24]. NMR samples were prepared as follows: appropriate amounts of biotransformation products and α-cyclodextrin were dissolved in 600 μL of D_2O (specific data in Table 1). Then the solutions were adjusted to proper pH (Table 1). Thereafter the measurement was done.

2.6. Absolute configuration assignment

The absolute configuration was assigned by measurements of the optical rotation $[\alpha]_{578}^{20}$ in 1 M NaOH. The results were evaluated and confirmed according to literature data [25]: $[\alpha]_{578}^{20} = -1.0$ for (*R*)-1-amino-2-methylpropanephosphonic acid; $[\alpha]_{578}^{20} = +18.0$ for (*S*)-1-aminophenylmethanephosphonic acid; $[\alpha]_{578}^{20} = +37.0$ for (*R*)-1-amino-2-phenylethanephosphonic acid.

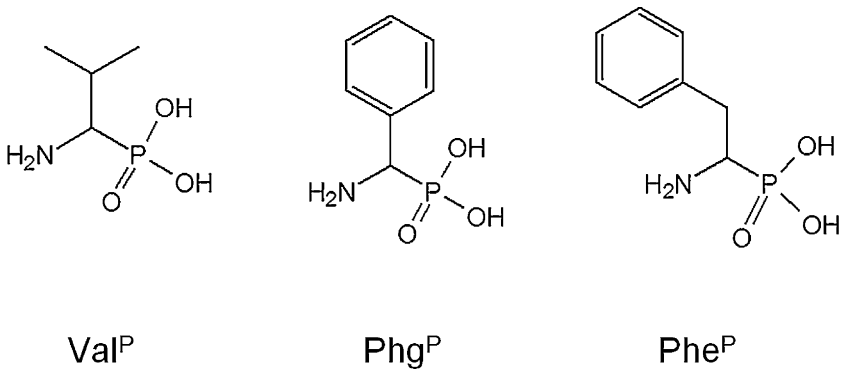

Fig. 2. Biotransformed α-aminophosphonic acids.

3. Results and discussion

The purpose of this research was to obtain optically pure enantiomers of α-aminophosphonic acids via microbial transformation of racemic mixture of chiral substrates, which is considered as kinetically controlled bioconversion. Several asymmetric synthesis methods for α-aminophosphonic acids derivatives have been developed so far [13,26–28]. The main strategies involve enantioselective and diastereoselective hydrophosphonylation of imines; enantioselective and diastereoselective reaction of aldehyde/ketone with amine and dialkyl phosphite; diastereoselective alkylation of phosphoglycinates derivatives; diastereoselective amination of phosphonates; chiral pool processes; catalytic asymmetric hydrogenation of dehydroaminophosphonates and resolution methodologies. Procedures developed until 2012 for the stereoselective synthesis of α-aminophosponic acids analogs of valine and phenylalanine were reviewed by Ordóñez et al. [29], whereas asymmetric synthesis methods concerning the analog of phenylglycine were reported by Joly and Jacobsen [30], Chen and Yuan [31], Abell and Yamamoto [32], Metlushka et al. [33], Zhao et al. [34] and Ohara et al. [35].

Relevant disadvantages of asymmetric synthesis (toxic wastes, organic solvents, catalysts, economy) make biocatalysis an interesting alternative. However, obtaining α-aminophosphonic acids via enzymatic resolution is still only partly explored field of biotechnology. Chenault et al. reported the application of Acylase I for the kinetic resolution of amino acids and their analogs with high enantiomeric excesses. However, that method was not applicable for α-aminophosphonic acids [36]. Solodenko et al. applied penicillin acylase for stereoselective hydrolysis of racemic 1-(N-phenylacetylamino)alkylphosphonic acids. Subsequently, the corresponding L-aminophosphonic acid was separated by column chromatography and acid hydrolysis of unreacted D-enantiomer allowed obtaining D-aminophosphonic acid [37].

Especially noteworthy is applying of whole-cell biocatalysts, because this strategy eliminates the necessity of using additional cofactors required by many enzymes. Microorganisms have the ability to perform diversified chemical reactions, most of them are very selective. Fungi are important source of enzymes of varied activities, some of them are commercially useful. Moreover, among these microorganisms, there are also strains able to biodegrade organophosphorus compounds by cleaving C—P bond. Some fungi utilize phosphonates as sole source of phosphorus for growth [20,38,39], therefore they are not susceptible to potential toxicity of these compounds. That is why chosen fungal strains were applied as biocatalysts, which implied in obtaining pure enantiomers of α-aminophosphonic acids – bioconversion substrates.

Presented studies are continuation of previous ones, which proved that, appropriate biotransformation conditions are crucial for the effectiveness of resolution of racemic mixtures of chiral xenobiotics with P—C bond, however in earlier research, only one model compound was examined and obtained optical purity was moderate – 50% of e.e. [40]. Therefore, current work extends these experimental field in order to improve the results, to find efficient microbial biocatalysts capable to resolve racemic mixtures of series of structurally different chiral α-aminophosphonates (Fig. 2), and finally to optimize the process conditions.

Among whole-cell biocatalysts tested, the most potent were two different strains of *F. oxysporum* (Table 2).

It should be pointed out, that the influence of cultivation conditions on bioconversion results, was significant. Application of Czapek-Dox Medium or special, rich medium containing inducer (compound mediating the amino acids transport cross plasma membrane and/or synthesis of enzymes of desired activity; here: amino acid oxidases) for growing *F. oxysporum* strain (UW1), implied in unsatisfactory results (enantiomeric excess up to 20%). In contradiction for the same fungal strain, direct addition of the substrate into the bioreaction medium, after the biomass cultivation on Potato Dextrose Broth for 3 days, fruited in obtaining of (*S*)-1-aminophenylmethanephosphonic acid and (*R*)-1-amino-2-phenylethanephosphonic acid as pure enantiomers (Fig. 3).

Furthermore, applying *F. oxysporum* strain (DSM 12646) cultivated on Malt Extract Peptone Broth resulted in obtaining pure (*R*)-1-amino-2-methylpropanephosphonic acid. What is important, the preincubation of that biocatalyst for 24 h under starvation conditions, before biotransformation, was crucial. It could arise from the fact, that this compound is not a physiological substrate

Table 2
Resolution of racemic mixtures of chiral α-aminophosphonic acids.

Substrate	The best results of biotransformation (e.e./configuration)	Substrate conversion [%]
Val^P	40% *R* (*Trigonopsis variabilis*)	29
	100% *R* (*Fusarium oxysporum* DSM 12646[a])	**50**
Phg^P	36% *S* (*Aspergillus niger*)	26
	27% *S* (*Aspergillus niger*[a])	21
	40% *R* (*Fusarium oxysporum* DSM 12646)	27
	54% *S* (*Fusarium oxysporum* DSM 12646[a])	33
	100% *S* (*Fusarium oxysporum* UW1)	**50**
	21% *S* (*Fusarium oxysporum* UW1[a])	16
Phe^P	19% *S* (*Fusarium oxysporum* DSM 12646)	16
	15% *R* (*Fusarium oxysporum* DSM 12646[a])	12
	100% *R* (*Fusarium oxysporum* UW1)	**50**

Bold was applied to indicate, when the racemic mixtures were completely resolved.
[a] Biotransformation procedure involved starvation step.

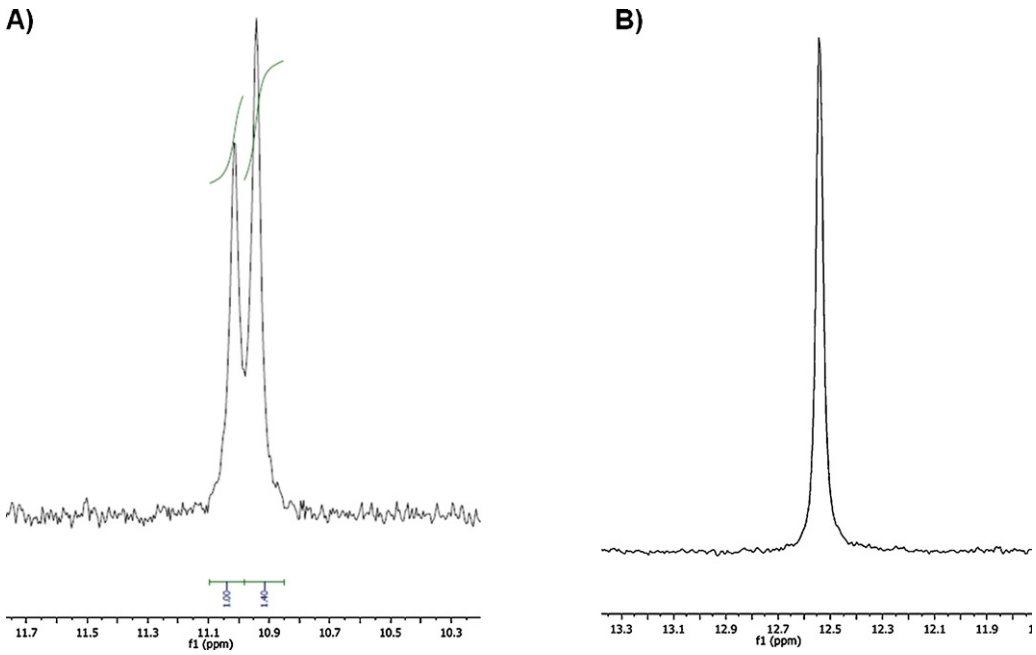

Fig. 3. ^{31}P NMR spectra of biotransformation products recorded with α-cyclodextrin: biocatalyst: *Fusarium oxysporum* strain (UW1) cultivated on PDB; substrate: 1-aminophenylmethanephosphonic acid: (A) first day of biotransformation – 17% e.e. of S-enantiomer, (B) third day of biotransformation – only *S*-isomer of 1-aminophenylmethanephosphonic acid is present.

for fungi, therefore, it is utilized only if other substances are not available. However, it is not a general phenomenon and conditions should be established empirically.

On the other hand, in the case of *F. oxysporum* strain (DSM 12646) the influence of starvation period on the absolute configuration of product was evident. When fresh cells were used, the enantiomeric excess after 3 days of biotransformation was 40% of *R*-enatiomer of phenylglycine analog and 19% of *S*-enatiomer of the phosphonic analog of phenylalanine. Applying cells preincubated in distilled water (starvation step) resulted in enrichment of racemic mixtures with the *S*-enatiomer of Phg^{P} (54% e.e.) and *R*-enatiomer of Phe^{P} (15% e.e.), respectively. Unfortunately, even when the biotransformation was carried out for 7 days, these mixtures were not completely resolved.

The analysis of ^{31}P NMR spectra of biotransformation mixture suggests possible mechanism of presented microbial conversion. Apart from signals corresponding to the products, there are no signals of other organophosphorus compounds. Probably, one enantiomer of α-aminophosphonic acid is transformed into α-ketophosphonic acid, which is unstable in water. The second one – unreacted – remains in the supernatant solution, that allows receiving optically pure α-aminophosphonic acid (Fig. 4). It could suggest, that amino acid oxidase is involved in the reaction. This enzyme under physiological conditions catalyzes the oxidative deamination of amino acids into corresponding α-keto acids [41–43]. There are L- and D-amino acid oxidases inside viable cells, which are absolutely stereoselective and transform only one, appropriate enantiomer. Thus, they can be used in processes leading to enantiomerically pure amino acids [44]. On the other hand, these enzymes show broad substrate specificity and are capable to deaminate several amino acids with hydrophobic side chains, and even some other chemical compounds such as cephalosporin C [43,45,46]. That is why, also α-aminophosphonic acids, as analogs of amino acids are possible substrates for amino acids oxidases. Other explanation of discussed lack of the signals deriving from other organophosphorus molecules, is that, the particular enantiomer – bioconversion substrate – is transported across plasma membrane and converted inside the cell, therefore the possibility of the transfer limits the process, living the optical purity of the products on moderate level. Finally it should be under consideration

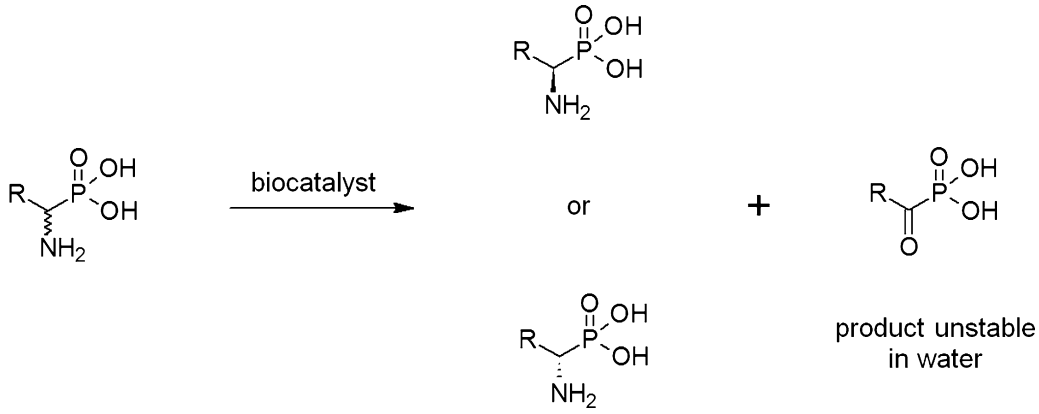

Fig. 4. Postulated mechanism of biotransformation.

that, despite other explanations, unstable oxoaminophosphonates (deamination step products) split and served as inorganic source of phosphorus atom for living cells and as a consequence any trace of phosphorus was recorded.

4. Conclusions

Assuming, this article reports for the first time protocols allowed obtaining pure enantiomers of α-aminophosphonic acids by applying whole-cell biocatalysts. Presented method is relatively simple and very efficient. It allows resolving racemic mixtures of phosphosphonic acid analogs of valine, phenylalanine and phenylglycine. Described procedure seems to be promising for scaling up and further application as an interesting alternative for asymmetric synthesis. Presented results constituted very important input in the chemoenzymatic synthesis of chiral phosphonates derivatives of biological importance.

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