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ORIGINAL ARTICLE

On the complexation of some univalent cations with beauvericin in nitrobenzene saturated with water

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Abstract From extraction experiments and γ-activity measurements, the exchange extraction constants corresponding to the general equilibrium $M^+(aq) + \mathbf{1}{\cdot}Cs^+(nb) \leftrightarrows \mathbf{1}{\cdot}M^+(nb) + Cs^+(aq)$ taking place in the two-phase water–nitrobenzene system ($M^+ = Li^+$, Na^+, K^+, Rb^+, H_3O^+, $NH_4{}^+$, Tl^+; $\mathbf{1}$ = beauvericin; aq = aqueous phase, nb = nitrobenzene phase) were determined. Moreover, the stability constants of the $\mathbf{1}{\cdot}M^+$ complexes in water-saturated nitrobenzene were calculated; they were found to increase in the series of $Rb^+ < Na^+$, $H_3O^+ < Tl^+ < NH_4^+ < K^+ < Li^+$.

Keywords Univalent cations · Beauvericin · Complexation · Extraction and stability constants · Water–nitrobenzene system

Introduction

Beauvericin (abbrev. **1**; see Scheme 1) [1] is a depsipeptide with antibiotic and insecticidal effects belonging to the enniatin family. It was isolated from the fungus *Beauveria bassiana*, but it is also produced by other fungi, including several *Fusarium* species [2]; it may therefore occur in grain (such as corn, wheat, and barley) contaminated with these fungi [2–4]. Beauvericin is active against gram-positive bacteria and mycobacteria, and it is also capable of inducing programmed cell death in mammals as well [2]. Chemically, beauvericin is a cyclic hexadepsipeptide with alternating methyl-phenylalanyl and hydroxy-iso-valeryl residues. Its ion-complexing capability allows beauvericin to transport alkaline earth metal and alkali metal ions across cell membranes.

The dicarbollylcobaltate anion (DCC^-) [5] and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs^+, Sr^{2+}, Ba^{2+}, Eu^{3+}, and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes [6–16], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste [17, 18].

In the current work, the solvent extraction of Li^+, Na^+, K^+, Rb^+, H_3O^+, $NH_4{}^+$, and Tl^+ into nitrobenzene by using a synergistic mixture of cesium dicarbollylcobaltate and beauvericin (see Scheme 1) was investigated. Furthermore, the stability constants of the proved univalent cation

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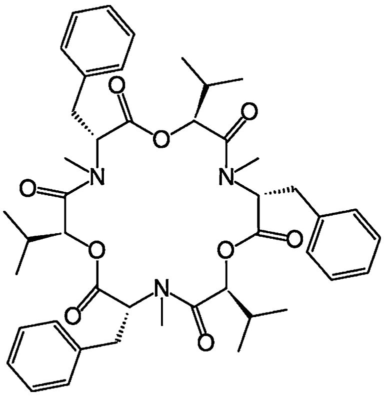


Scheme 1 Structural formula of beauvericin (abbrev. **1**)

complexes with the mentioned beauvericin ligand **1** were evaluated in the organic phase of the water–nitrobenzene extraction system.

Experimental

Beauvericin (abbrev. **1**) was purchased from Aldrich. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [19]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{137}Cs^+$ (Techsnaveksport, Russia) was of standard radiochemical purity.

The extraction experiments were carried out in 10-mL polypropylene test-tubes with polypropylene stoppers: 2 mL of an aqueous solution of MNO_3 ($M^+ = Li^+$, Na^+, K^+, Rb^+, H^+, NH_4^+, Tl^+) of the concentration in the range from 1×10^{-2} to 3×10^{-2} M and microamounts of $^{137}Cs^+$ were added to 2 mL of a nitrobenzene solution of **1** and CsDCC, the initial concentrations of which also varied from 1×10^{-2} to 3×10^{-2} M (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{in,nb}$, was equal to the initial concentration of CsDCC in this medium, $C_{CsDCC}^{in,nb}$). The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of cesium, D_{Cs}, were determined as the ratios of the measured radioactivities of $^{137}Cs^+$ in the nitrobenzene and aqueous samples.

Results and discussion

Regarding the results of previous papers [5, 20, 21], the two-phase water–MNO_3 ($M^+ = Li^+$, Na^+, K^+, Rb^+, H_3O^+, NH_4^+, Tl^+)–nitrobenzene–CsDCC extraction system can be described by the following equilibrium

$$M^+(aq) + Cs^+(nb) \leftrightarrows M^+(nb) + Cs^+(aq);\ K_{ex}(M^+, Cs^+) \tag{1}$$

with the corresponding exchange extraction constant K_{ex} (M^+, Cs^+); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant K_{ex} (M^+, Cs^+) one can write [5, 20, 21]

$$\log K_{ex}(M^+,\ Cs^+) = \log K^i_{M^+} - \log K^i_{Cs^+} \tag{2}$$

where $K^i_{M^+}$ and $K^i_{Cs^+}$ are the individual extraction constants for M^+ and Cs^+, respectively, in the water–nitrobenzene system [20, 21]. Knowing the values $\log K^i_{M^+}$ ($M^+ = Li^+$, Na^+, K^+, Rb^+, H_3O^+, NH_4^+, Tl^+) [20, 21], the single exchange extraction constants K_{ex} (M^+, Cs^+) were simply calculated from Eq. 2. The corresponding data are given in Table 1.

Previous results [22–26] indicated that the two-phase water–MNO_3 ($M^+ = Li^+$, Na^+, K^+, Rb^+, H_3O^+, NH_4^+, Tl^+)–nitrobenzene–**1** (beauvericin)–CsDCC extraction system (see Experimental Section), chosen for determination of the stability of the $\mathbf{1}\cdot M^+$ complex in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (3):

$$M^+(aq) + \mathbf{1}\cdot Cs^+(nb) \leftrightarrows \mathbf{1}\cdot M^+(nb) + Cs^+(aq);\ K_{ex}(M^+, \mathbf{1}\cdot Cs^+) \tag{3}$$

with the general equilibrium extraction constant K_{ex} (M^+, $\mathbf{1}\cdot Cs^+$):

$$K_{ex}(M^+,\ \mathbf{1}\cdot Cs^+) = \frac{[\mathbf{1}\cdot M^+]_{nb}[Cs^+]_{aq}}{[M^+]_{aq}[\mathbf{1}\cdot Cs^+]_{nb}} \tag{4}$$

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where it forms the relatively stable complexes $\mathbf{1}\cdot M^+$ with the mentioned univalent cations. Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the univalent cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured distribution ratio of cesium, $D_{Cs} = [\mathbf{1}\cdot Cs^+]_{nb}/[Cs^+]_{aq}$, combined with Eq. 4, we obtain the final expression for K_{ex} (M^+, $\mathbf{1}\cdot Cs^+$) in the form

$$K_{ex}(M^+,\ \mathbf{1}\cdot Cs^+) = \frac{1}{D_{Cs}}\ \frac{C_{CsDCC}^{in,nb}}{(1 + D_{Cs})\ C_{MNO_3}^{in,aq} - C_{CsDCC}^{in,nb}} \tag{5}$$

where $C_{MNO_3}^{in,aq}$ is the initial concentration of MNO_3 ($M^+ = Li^+$, Na^+, K^+, Rb^+, H_3O^+, NH_4^+, Tl^+) in the aqueous phase and $C_{CsDCC}^{in,nb}$ denotes the initial concentration

Table 1 Equilibrium data for the M^+ and $\mathbf{1}\cdot M^+$ cations in the two-phase water–nitrobenzene extraction system at 25 °C (M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+, H_3O^+, NH_4^+, Tl^+; **1** = beauvericin; for the meaning of the constants see text)

Quantity	M^+							
	Li^+	Na^+	K^+	Rb^+	Cs^+	H_3O^+	NH_4^+	Tl^+
$\log K^{i}_{M^+}$ [a]	−6.7	−6.0	−4.1	−3.4	−2.7	−5.7	−4.7	−3.4[b]
$\log K_{ex}$ (M^+, Cs^+)[c]	−4.0	−3.3	−1.4	−0.7	–	−3.0	−2.0	−0.7
$\log K_{ex}$ (M^+, $\mathbf{1}\cdot Cs^+$)[d,g]	−2.3	−2.8	−0.5	−0.3	–	−2.5	−1.3	−0.1
$\log \beta_{nb}$ ($\mathbf{1}\cdot M^+$)[e,g]	5.6	4.4	4.8	4.3	3.9[f]	4.4	4.6	4.5

[a] Ref. [20]

[b] Ref. [21]

[c] Calculated from Eq. 2 using data from Refs. [20, 21]

[d] Calculated from Eq. 5

[e] Calculated from Eq. 6 using data from Refs. [20, 21, 31]

[f] Ref. [31]

[g] The standard deviations of the constants $\log K_{ex}$ (M^+, $\mathbf{1}\cdot Cs^+$) and $\log \beta_{nb}$ ($\mathbf{1}\cdot M^+$) are lower than 0.1

of CsDCC in the organic phase of the system under consideration.

In this study, from the extraction experiments and γ-activity measurements (see Experimental Section) by means of Eq. 5, the logarithms of the constants K_{ex} (M^+, $\mathbf{1}\cdot Cs^+$) were determined, as given in Table 1.

Moreover, with respect to Refs. [22–26], for the extraction constants K_{ex} (M^+, Cs^+) and K_{ex} (M^+, $\mathbf{1}\cdot Cs^+$) defined above, as well as for the stability constants of the complexes $\mathbf{1}\cdot M^+$ and $\mathbf{1}\cdot Cs^+$ in nitrobenzene saturated with water, denoted by β_{nb} ($\mathbf{1}\cdot M^+$) and β_{nb} ($\mathbf{1}\cdot Cs^+$), respectively, one gets

$$\log\beta_{nb}(\mathbf{1}\cdot M^+) = \log\beta_{nb}(\mathbf{1}\cdot Cs^+) + \log K_{ex}(M^+, \mathbf{1}\cdot Cs^+) - \log K_{ex}(M^+, Cs^+) \qquad (6)$$

By using the values of $\log K_{ex}$ (M^+, Cs^+) and $\log K_{ex}$ (M^+, $\mathbf{1}\cdot Cs^+$) given in Table 1, $\log \beta_{nb}$ ($\mathbf{1}\cdot Cs^+$) = 3.9 [31], and applying Eq. 6, the stability constants of the $\mathbf{1}\cdot M^+$ complexes ($M^+ = Li^+$, Na^+, K^+, Rb^+, H_3O^+, NH_4^+, Tl^+) in water-saturated nitrobenzene were evaluated. These data are also listed in Table 1. Thus, the $\log \beta_{nb}$ ($\mathbf{1}\cdot M^+$) values from this table indicate that the stability of the $\mathbf{1}\cdot M^+$ cationic complex species in the mentioned nitrobenzene medium increases in the following cation order: $Cs^+ < Rb^+ < Na^+, H_3O^+ < Tl^+ < NH_4^+ < K^+ < Li^+$.

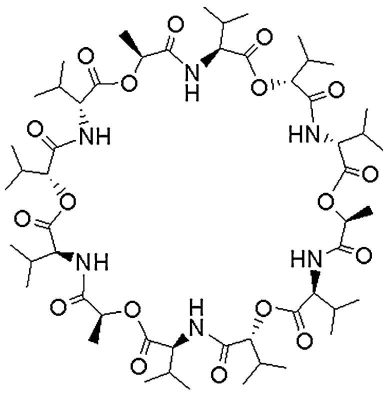
Finally, Table 2 summarizes stability constants of the cationic complexes $\mathbf{2}\cdot M^+$, where $M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+, H_3O^+, NH_4^+, Tl^+ and **2** denotes the valinomycin ligand (see Scheme 2), determined previously in water-saturated nitrobenzene as well [23–30]. From comparison of the data reviewed in Tables 1 and 2 it follows that in the considered nitrobenzene medium, the stability of the $\mathbf{1}\cdot M^+$ complex species ($M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+, H_3O^+, NH_4^+, Tl^+) is always lower than that of the corresponding cationic complex $\mathbf{2}\cdot M^+$ with the same central cation M^+.

In conclusion, it should be noted that in the case of cyclic polyether compounds with oxyethylene groups $-CH_2-CH_2-O-$, that are called crowns owing to their structure [32, 33], as well as in the case of valinomycin [34], the ratio of the size of the ligand cavity to the ion radius of the central cation is a decisive or at least an important factor in the stability of the complex species formed [34]. On the other hand, the diameter of the beauvericin ligand cavity (cca 6.5 Å; 1 Å = 0.1 nm) [1] evidently does not play the crucial role in the stability of the univalent cationic complexes under study, as follows from the values of the stability constants reviewed in Table 1. However, somewhat higher stability constant of the Li^+ complex with the considered beauvericin ligand **1**—in comparison with the remaining stability constants presented in Table 1—could be probably explained by stabilization of this lithium complex by some (e.g., by three) water molecules in nitrobenzene saturated with water, analogously as in Ref. [27].

Table 2 Stability constants of the $\mathbf{2}\cdot M^+$ complexes (**2** = valinomycin; M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+, H_3O^+, NH_4^+, Tl^+) in nitrobenzene saturated with water at 25 °C

M^+	Li^+	Na^+	K^+	Rb^+	Cs^+	H_3O^+	NH_4^+	Tl^+
$\log \beta_{nb}$ ($\mathbf{2}\cdot M^+$)	6.3[a]	6.7[b]	10.6[c]	11.7[d]	10.1[e]	5.3[f]	8.4 [g]	10.1 [h]

[a] Ref. [27], [b] Ref. [25], [c] Ref. [28], [d] Ref. [24], [e] Ref. [23], [f] Ref. [26], [g] Ref. [29], [h] Ref. [30]



Scheme 2 Structural formula of valinomycin (abbrev. **2**)

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