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ORIGINAL ARTICLE

Synthesis and amino acid extraction abilities of chiral calix[4]arene triamides containing amino alcohol units

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Abstract Herein the synthesis and extraction abilities of new D-/L-phenylalaninol substituted *p-tert*-butylcalix[4]arene triamide derivatives (**3** and **4**) towards amino acids are reported. These compounds (**3** and **4**) have been easily synthesized via aminolysis of *p-tert*-butylcalix[4]arene trimethylester (**2**) with D-/L-phenylalaninol in methanol-toluen solvent system at one step. The extraction properties of the prepared chiral calix[4]arene triamide derivatives (**3** and **4**) towards some selected amino acid methylesters are studied by liquid–liquid extraction. Results show that these chiral calix[4]arene triamide derivatives (**3** and **4**) exhibited a good affinity towards all amino acid species without any remarkably discrimination.

Keywords Calix[4]arene · Triamide · Amino acids · Liquid–liquid extraction

Introduction

Calixarenes, cyclic oligomers of phenolic units linked through the ortho positions, are a fascinating class of macrocycles. They are synthetic macrocycles readily available by condensation of *p-tert*-butylphenol with formaldehyde under alkaline conditions. From these starting materials, a large number of sophisticated compounds have been prepared. To date, various calixarenes that possess ketone, amine, ester, amide, carboxylic acid or other functional groups have been synthesized for separation, recognition, discrimination and catalysis. A number of books were published concerning synthesis, structural features and host-guest interactions [1]. More specifically, the subject of chemical recognition and separation of ions was addressed in several publications [2]. On the other hand, only few reviews concerning calixarenes for biochemical recognition are available, e.g. on peptido- and glycoconjugates and the role of hydrogen-bonding interactions [3], on neoglyco conjugates with large rigidified cavities [4] and on synthetic receptors [5]. Among them, chiral recognition, the process in which an enantiomerically pure host molecule, such as a chiral calixarene, selectively binds one of the enantiomers, is one of the most essential reaction processes occurring in living systems [6]. Therefore chiral calixarenes [7] have attracted increasing research interest because of their potential in enantio discrimination processes. They can be obtained either by attaching chiral moieties at one of the calix rims (upper or lower) [1] or by synthesizing inherently chiral derivatives [8] in which an asymmetric substitution of the macrocycle is associated to its intrinsic three-dimensional nature. From a practical point of view, the first approach appears to be preferable because inherent chirality always requires a difficult resolution on an appropriate scale [9]. Therefore, a large number of chiral calixarenes have been prepared by using chiral units, such as single amino acids [10], peptides [11], amino alcohols [12], sugars [13], tartaric acid esters [14], binaphthyl [15], glycidyl [16], menthone [17], and guanidinium groups [18].

Very recently, we have reported the synthesis of two chiral calix[4]arenes bearing *R-/S*-phenyl ethylamine moieties and two chiral calix[6]arenes bearing D-/L-phenylalaninol groups, and the evaluation of their extraction ability towards some amino acid methylesters [19a, b]. In addition, generally, it has been used the diamide derivatives of calixarene for amino acid extraction studies, whereas the

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triamide derivatives of calixarene have not been studied until now, according to our knowledge. We think that it could be interesting for the goal of amino acid recognition and discrimination. Therefore we report the synthesis of the chiral calix[4]arene amide derivatives bearing D-/L-phenylalaninol group and their use as ligands in amino acid extraction studies.

Results and discussion

Synthesis

In this study, we report the synthesis of chiral calix[4]arene triamide derivatives using commercially available, inexpensive chiral amino alcohols. We also explore the extraction abilities of chiral calix[4]arene amide derivatives **3** and **4** towards some selected α-amino acid methylesters via the two phase solvent extraction system. To achieve this, the trimethylester derivative (**2**) of *p-tert*-butylcalix[4]arene (**1**) has been chosen as a precursor. The synthesis of compound **1**and its trimethylester derivative (**2**) has been performed according to previously described methods [20, 21]. Therefore the compounds **3** and **4** are reported for the first time in this study. The synthetic route has been conducted as shown in Fig. 3.

In the synthesis of *p-tert*-butylcalix[4]arene triamides, the aminolysis reaction of *p-tert*-butylcalix[4]arene trimethylester (**2**) is a simple method [22a, b, 23]. Thus, according to the strategy outlined in Fig. 3, 5,11,17,23-*tert*-butyl-25,26,27-methoxycarbonylmethoxy-28-hydroxy calix[4]arene **2** has been refluxed with D-/L-phenylalaninol in toluene/methanol (1:1) solvent mixture to give the corresponding triamide derivatives of *p-tert*-butylcalix[4]arene **3** and **4** in 45% and 48% yields, respectively. It is important that the chiral triamides have been directly synthesized at only one step from trimethylester **2**. Generally in the literature [24, 25, 26] the calixarene amide derivatives can be synthesized at three steps via conversion of the ester to acid, acid chloride and amide, respectively.

The new compounds **3** and **4** have been characterized by a combination of ^{1}H NMR, FTIR, FAB MS, and elemental analysis. The formation of the chiral triamide derivatives of *p-tert*-butylcalix[4]arene **3** and **4** have been confirmed by the appearance of the characteristic amide bands at 1664 cm^{-1} and 1660 cm^{-1}, respectively, by the disappearance of the ester carbonyl band at about 1765 cm^{-1} in their IR spectra. The conformational characteristics of calix[4]-arenes have been conveniently estimated by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^{1}H NMR spectroscopy [1]. ^{1}H NMR data showed that compounds **3** and **4** have a cone conformation. A typical AB pattern has been observed for the methylene bridge $ArCH_2Ar$ protons at 3.02 (J = 13 Hz), 4.41 (J = 13 Hz), 4.51 (J = 13 Hz) for **3** and at 3.09 (J = 13 Hz), 4.38 (J = 13 Hz), 4.55 (J = 13 Hz) for **4** in ^{1}H NMR.

Two-phase solvent extraction studies

The present work is focused to elaborate the strategic requirements for the two-phase extraction measurements, therefore, the binding abilities of parent *p-tert*-butylcalix[4]arene **1**, its trimethylester derivative **2** and its chiral triamide derivatives **3** and **4** toward some selected amino acids have been evaluated by means of solvent extraction of their ammonium picrates and the results have been summarized in Table 1. These data have been obtained by using ligands in dichloromethane solution to extract ammonium picrates from its aqueous solutions. The equilibrium concentration of ammonium picrate in aqueous phase has been then determined spectrophotometrically. From the extraction data given Table 1, it has been observed that parent *p-tert*-butylcalix[4]arene **1** and trimethylester derivative **2** transfer all amino acid species from aqueous phase into organic phase in trace amounts, and chiral calix[4]arene triamides **3** and**4** recognize all amino acid species in high yields. According to our experience and knowledge from our previous study and the other studies [19a, b, 27], increased extraction properties of chiral calix[4]arene amides (**3** and **4**) can be explained by multiple hydrogen bonding between chiral calix[4]arene triamides and amino

Table 1 Extraction percentage of selected amino acid methylesters with **1**, **2**,**3** and **4**[a]

Ligand	D-AlaOMe	L-AlaOMe	D-PheOMe	L-PheOMe	D-TrpOMe	L-TrpOMe
1[b]	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
2	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
3	54.1	56.5	71.3	68.5	68.4	69.7
4	59.5	57.4	65.8	67.5	62.6	68.3

[a] Aqueous phase, [ammonium picrate] = 2.0×10^{-5} M; organic phase, dichloromethane, [ligand] = 1.0×10^{-3}; at 25 °C, for 1 h

[b] Chloroform was used as organic phase

acids moieties. In addition, the guests are stabilized by CH-π interactions with the aromatic walls of the hydrophobic cavity of the chiral calix[4]arenes (**3** and **4**). Also in order to eliminate Pic-driven extraction, blank tests for the extraction of a tetrabutylammonium picrate and picric acid by using ligands were performed. From the results it was appeared that ligands complexed with tetrabutylammonium picrate but not with picric acid. This confirms that there is no effect of picrate in the extraction process.

Furthermore, an expectation of this study is also to observe a chiral discrimination between amino acid molecules by using these new chiral calix[4]arene triamides as ligand. However they do not show remarkable chiral discrimination between these amino acids.

The extraction data for **4** has been analyzed by a classical slope analysis method. Assuming the extraction of an ammonium cation ($R\text{-}NH_3^+$) by the receptor **4** according to the following equilibrium:

$$[R\text{-}NH_3^+]_{aq} + [Pic^-]_{aq} + x[L]_{org} \overset{K_{ex}}{\rightleftharpoons} [R\text{-}NH_3Pic(L)_x]_{org} \quad (1)$$

The extraction constant K_{ex} is then defined by:

$$K_{ex} = \frac{[R\text{-}NH_3Pic(L)_x]_{org}}{[R\text{-}NH_3^+]_{aq}[Pic^-]_{aq}[L]_{org}^x} \quad (2)$$

The distribution ratio D_A is defined as ratio of the concentrations of the ammonium cation ($R\text{-}NH_3^+$) in the two phases:

$$D_A = [R\text{-}NH_3Pic(L)_x]_{org}/[R\text{-}NH_3^+]_{aq}[Pic^-]_{aq} \quad (3)$$

Thus Eq. 2 can be rewritten as:

$$\log D_A = \log K_{ex} + x\log [L] \quad (4)$$

Consequently a plot of log D_A versus log [L] leads to a straight line whose slope allows the stoichiometry of the extracted species to be determined.

Figure 1 represents the extraction into dichloromethane at different concentrations of **4** for the ammonium ion. A linear relationship between log D_A versus log [L] is observed with a slope for ammonium ion by **4** which equals 1.96, suggesting that **4** forms a 2:1 complex with an ammonium cation. The analytical data of **4** shows that the complexation reaction takes place according to the following equilibrium:

$$2(L)_{org} + (R\text{-}NH_3^+Pic^-)_{aq} \overset{K_{ex}}{\rightleftharpoons} (L_2,\ R\text{-}NH_3^+Pic^-)_{org} \quad (5)$$

According to experimental data, if the Eq. 2 rearrangement for **6**, log K_{ex} has the value 6.11 ± 0.2.

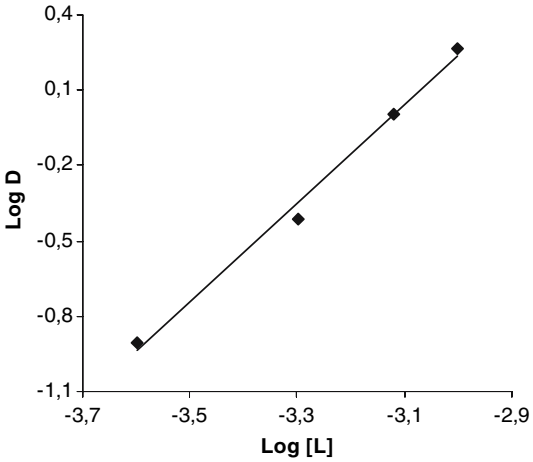

Fig. 1 Log D versus log [L] for the extraction of D-PheOMe by **4** from an aqueous phase into dichloromethane phase at 25 °C

Conclusion

A trimethylester derivative of *p-tert*-butylcalix[4]arene (**2**) was converted to its triamide derivative with chiral amino alcohol groups to observe the chiral extraction abilities towards some selected amino acids. Although the chiral calix[4]arene triamide derivatives (**3** and **4**) were excellent extractants for all used amino acid species, the chiral discrimination between amino acid molecules could not be obtained. It had been noted that the hydrophobic cavity of chiral calix[4]arenes and hydrogen bonding lead to recognize these amino acid species and also the chiral calix[4]arene triamide derivatives (**3** and **4**) have been easily synthesized at only three steps. This work would be contribute to the synthesis of chiral and enantioselective receptors.

Experimental

Materials and general methods

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ with TMS as internal standard. FTIR spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. UV–vis. spectra were obtained on a Shimadzu 160A UV–visible recording spectrophotometer. FAB-MS spectra were taken on a Varian MAT 312 spectrometer. Elemental analyses were performed on a Leco CHNS-932 analyzer. Specific rotations were measured on A Krüss Optronic polarimeter.

Thin layer chromatography was performed on precoated silica gel plates (SiO_2, Merck PF_{254}), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230—240 mesh) was used for preparative column chromatography. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Acetone was distilled from $CaSO_4$. All aqueous solutions were prepared with deionized water passed through a Millipore Milli-Q Plus water purification system.

Amino acid methylester hydrochlorides given in Fig. 2 were obtained from Aldrich or Merck at the highest purity commercially available and were used in this study: L-phenylalanine methylester hydrochloride (L-PheOMe), D-phenylalanine methylester hydrochloride (D-PheOMe), L-alanine methylester hydrochloride (L-AlaOMe), D-alanine methylester hydrochloride (D-AlaOMe), L-tryptophan methylester hydrochloride (D-TrpOMe) and D-tryptophan methylester hydrochloride (D-TrpOMe) (Fig. 2).

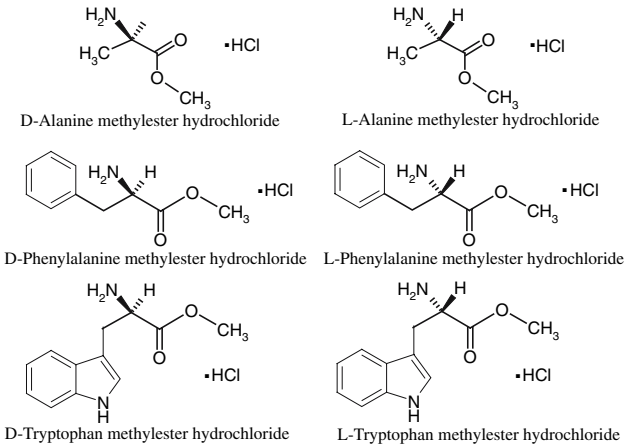

Fig. 2 The chemical structures of some selected amino acid methylesters used in experiments

Synthesis

Figure 3 illustrates the successive synthetic steps of the extractants (**1–4**) used. Compounds **1** and**2** were prepared according to literature methods [20, 21]. Other compounds (**3** and**4**) were synthesized by adapting from known aminolysis procedure [22a, b, 23].

General procedure for the synthesis of compounds **3** and **4**

An appropriate amino alcohol (20.0 mmol) was dissolved in 1:1 toluene/MeOH mixture (60 mL) and added dropwise to a solution of 5,11,17,23-tert-butyl-25,26,27-methoxycarbonylmethoxy-28-hydroxycalix[4]arene **2** and (4.0 mmol) in 20 mL toluene with continuous stirring at room temperature for about 30 min. The reaction mixture was

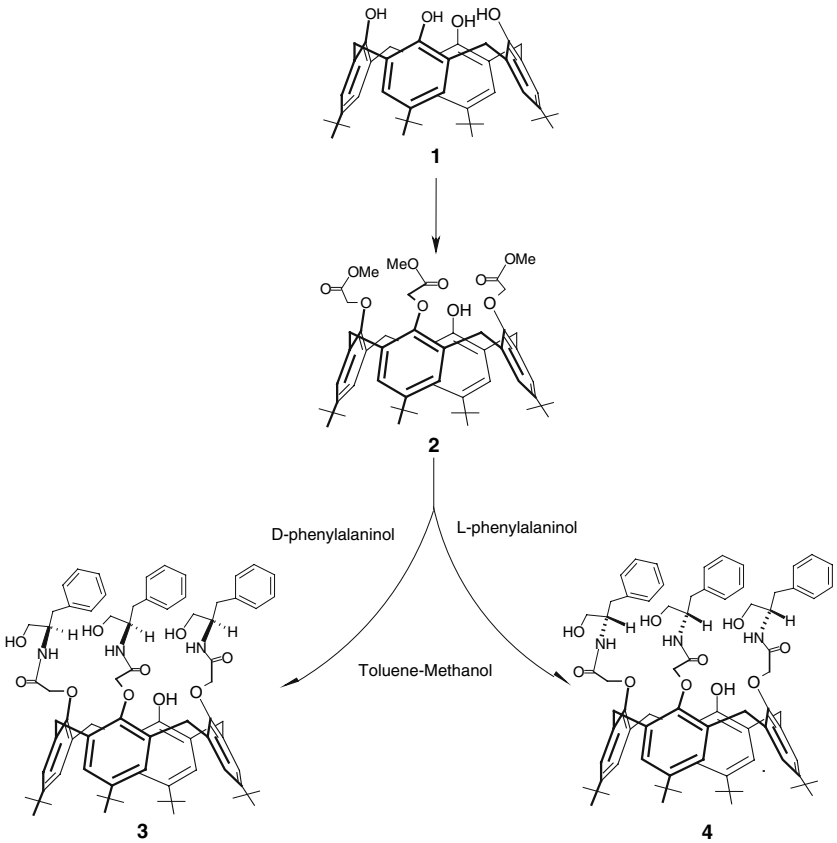

Fig. 3 Schematic representation of synthesis of chiral calix[4]arene triamide derivatives (**3** and **4**)

refluxed and the reaction was monitored by TLC. After the substrate had been consumed, the solvent was evaporated under reduced pressure and the residue triturated with MeOH to give a crude product. The crude products were purified by flash chromatography and recrystallized.

For compound **3**, yield: 45%, mp: 139 °C. $[\alpha]_D^{22}$ = –19.7° (*c* 3.3, $CHCl_3$); IR (KBr): 1664 cm^{-1} (NH=CO), 3380 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$): δ 0.83 (s, 18H, *tert*-butyl), 1.19 (s, 18H, *tert*-butyl), 2.87 (d, *J* = 7.0 Hz, 6H, CH CH_2Ar), 3.02 (d, *J* = 13.0 Hz, 4H, $ArCH_2Ar$), 3.19 (d, *J* = 15.0 Hz, 6H, CH_2OH), 3.65 (m, 3H, CH_2 $CHCH_2$), 4.08 (d, *J* = 11.0 Hz, 2H, $ArOCH_2$), 4.19 (s, 4H, $ArOCH_2$), 4.41 (d, *J* = 13.0 Hz, 2H, $ArCH_2Ar$), 4.51 (d, *J* = 13.0 Hz, 2H, $ArCH_2Ar$), 6.58 (s, 3H, CH_2 *OH*), 7.06 (s, 8H, ArH_{meta}), 7.13 (m, 15H, ArH_{phenyl}), 7.48 (s, 1H, ArOH), 8.22 (d, *J* = 8.0 Hz, 3H, NH). FAB-MS *m/z*: (1245.6) $[M+Na]^+$ (calcd 1245.6). Calculated for $C_{77}H_{95}N_3O_{10}$ (1222.59): C, 75.64; H, 7.83; N, 3.44. Found: C, 75.82; H, 7.94; N, 3.41.

For compound **4**, yield: 48%, mp: 137 °C. $[\alpha]_D^{22}$ = + 19.9° (*c* 3.3, $CHCl_3$); IR (KBr): 1660 cm^{-1} (NH=CO), 3402 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$): δ 0.85 (s, 18H, *tert*-butyl), 1.16 (s, 18H, *tert*-butyl), 2.85 (d, *J* = 7.0 Hz, 6H, $CHCH_2Ar$), 3.09 (d, *J* = 13.0 Hz, 4H, $ArCH_2Ar$), 3.23 (brs, 6H, CH_2OH), 3.62 (m, 3H, CH_2CHCH_2), 4.11 (d, *J* = 11.0 Hz, 2H, $ArOCH_2$), 4.23 (s, 4H, $ArOCH_2$), 4.38 (d, *J* = 13.0 Hz, 2H, $ArCH_2Ar$), 4.55 (d, *J* = 13.0 Hz, 2H, $ArCH_2Ar$), 6.54 (s, 3H, CH_2OH), 7.01 (s, 8H, ArH_{meta}), 7.15 (m, 15H, ArH), 7.44 (s, 1H, ArH_{phenyl}), 8.24 (d, *J* = 8.0 Hz, 3H, NH). FAB-MS *m/z*: (1245.6) $[M+Na]^+$ (calcd 1245.6). Calculated for $C_{77}H_{95}N_3O_{10}$ (1222.59): C, 75.64; H, 7.83; N, 3.44. Found: C, 75.84; H, 7.90; N, 3.40.

Analytical Procedure

Picrate extraction experiments were performed following Pedersen's procedure [28]. A 10 mL of a 2.0×10^{-5} M aqueous picrate (the picrate solutions were prepared as our previous study [19a]) and 10 mL of 1.0×10^{-3} M solution of calixarene (**2**, **3** and **4**) in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water-bath at 25 °C for 1 h, and finally left standing for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of calixarene. The percent extraction (E%) has been calculated as:

$$E\% = (A_o - A/A_o) \times 100 \quad (6)$$

where A_o and A are the initial and final concentrations of the ammonium picrate before and after the extraction, respectively.

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