



Monolithic silica columns with covalently attached octaproline chiral selector. Dependence of performance on derivatization degree and comparison with a bead-based analogue



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ARTICLE INFO

Article history:

Received 31 July 2014

Received in revised form 16 January 2015

Accepted 19 January 2015

Available online 28 January 2015

Keywords:

Poly-L-proline oligomers

Silica monoliths

Loadability

Enantioseparation

Chiral stationary phases

ABSTRACT

A monolithic silica gel chromatographic matrix was derivatized repetitively with an octaproline-derived chiral selector (CS). The increasingly derivatized column was tested after each derivatization reaction. The enantioseparation ability, resolution and efficiency were found to depend on the content of CS attained after each reaction. Moreover, enantioselectivity and performance of the column with the highest CS coverage were compared to those of a bead-based chiral stationary phase (CSP) counterpart. The octaproline-derivatized monolithic column demonstrated increased enantioseparation factors, resolution and broader applicability than the particle-based column. Finally, the loading capacity of the CSPs was also examined. The monolithic octaproline-derived column permits the separation of 3–20 times higher molar amounts of the tested analytes (depending on the compound considered) than the particle-based counterpart. The enhanced capabilities of the derivatized monolithic column with respect to that of a bead-based counterpart cannot be explained only on the basis of an increased CS coverage. The involvement of an effect produced by the chromatographic silica support structure in the obtained results is discussed.

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1. Introduction

As a result of the increasing demand of single enantiomers, chiral stationary phases (CSPs) have become a fundamental tool in the analysis and purification of this kind of isomers [1]. One of the most recent discoveries in enantioselective chromatography is the outstanding and, somehow, unforeseen enantioselectivity of polyproline-derived chiral selectors (CSs) [2–5]. Oligoproline-derived CSPs share some features in common with brush-type CSPs. The most remarkable is the relative low-molecular weight of the chiral selector (CS). However, oligoproline-based CSPs show a higher selectivity and a broader application domain than most brush-type CSPs [3]. These structures are considered to constitute a new class of peptide-based CSs [2]. Li and co-workers were the first authors to apply them in liquid chromatography CSPs [3–5].

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Our group was also interested in the enantioselection ability of this type of CSs. In previous studies, 3,5-dimethylphenylcarbamoyl-substituted oligoproline-derived bead-based CSPs were prepared [6,7]. A strong dependence of enantioselectivity on the type of mobile phase used was detected at this point. Subsequently, the enantioselectivity and performance of a non-substituted octaproline-derived particle-based CSP [8] was compared to that containing the substituted CS [6] using different mobile phases. The significance of CS conformation as well as the important role of H-bonding on enantioselectivity was confirmed. Most tested analytes bearing at least one H-bond donor group were better resolved on the non-substituted oligoproline-derived CSP. This enhanced enantioselectivity was attributed to the improved availability of the carbonyl groups on the octaproline CS due to the lack of the voluminous 3,5-dimethylphenylcarbamate groups. In parallel, poly-(4R)-(3,5-dimethylphenylaminocarbonyloxy)-L-proline CS was fixed to monolithic silica gel and the performance of the resulting CSP tested [9].

In situ chiral modification of silica monoliths has been already applied to the preparation of monolithic CSPs [10,11] as this format has acquired a significant relevance in high performance liquid

chromatography (HPLC) [9,12], capillary chromatography [13–15] and capillary electrochromatography (CEC) [16–19]. Monolithic matrices offer some advantages over bead-based supports. Among them the ease of preparation, high reproducibility, versatile surface modification, high permeability and good peak capacity [12,20] make them a good alternative to more classical bead-format matrices. Moreover, backpressures in monolithic beds can be maintained low even at high flow rates. In such conditions separation values are maintained while reducing retention, and consequently providing high-throughput and high productivity [21].

When the above mentioned substituted oligoproline CS was bonded to monolithic silica rods an improved chromatographic performance was obtained [9]. In spite of similar specific surface, monolithic silica permits a higher coverage of polyproline-based CSs onto the matrix than their particle-based counterparts. The resulting columns showed higher retention times, greater separation factors and a broader application domain than their bead-based counterparts.

On the basis of these observations, the aim of this study is to determine if the observed chromatographic improvement is a direct consequence of the increase of CS density on the monolithic with respect to the bead format and/or the consequence of an improved accessibility of the CS provided by the structure of the matrix. The evaluation of the influence of the degree of derivatization on the performance of monolithic columns will provide us with some insights on the specific role of the matrix format in this case. Given the higher enantioselectivity of non-substituted-oligoprolines over substituted-oligoprolines and the higher derivatization of the CSP when the CS lacks of bulky dimethylphenylcarbamate groups, a non-substituted-octaproline derivative was the CS chosen for this purpose (Fig. 1).

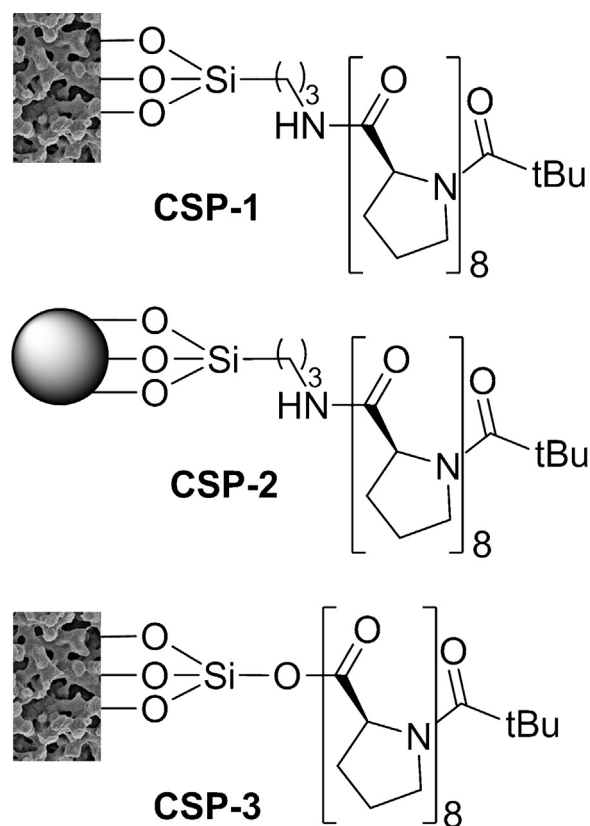


Fig. 1. Chemical structures of the CSPs in the study.

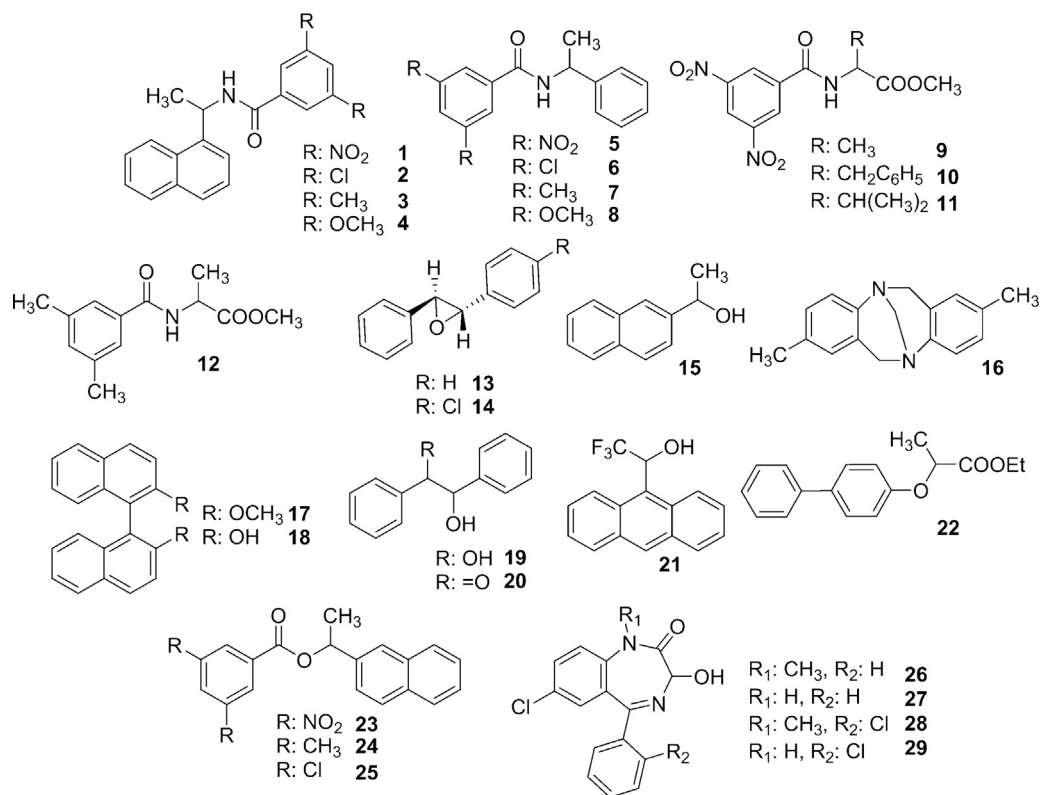


Fig. 2. Structures of the test compounds in the study.

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