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APPROACH OF USING THE OPPOSITE CHIRALITY OF CROWN ETHER STATIONARY PHASES IN CHIRAL RECOGNITION OF TETRAPEPTIDE ENANTIOMERS

Friday, 11 February 2022 13:00 (15 minutes)

Crown ether chiral stationary phases have been successfully used for separating enantiomers of various racemic compounds containing primary amino groups. Although chiral recognition mechanism for crown-ether CSPs is generally understood, on a molecular level, the exact chiral recognition mechanisms for the resolution of short peptides, containing multiple amino moieties capable of binding to the crown ether selector, are still unclear [1].
A research of relationship between the peptide chemical structure and chiral chromatographic interactions was performed, by comparing the retention profiles of μ-opioid receptor agonist tetrapeptide Tyr-Arg-Phe-Lys-NH2 and eight its structural analogues, synthesized with the aim to selectively exclude interacting amino groups in tetrapeptide sequence on S- and R-(3,3'-diphenyl-1,1′-binaphthyl)-20-crown-6) stationary phases [CR-I (+) and (-)], in order to clarify, which of the potential interaction sites are responsible for chiral recognition in Tyr-Arg-Phe-Lys-NH2 tetrapeptide.
It was established, that, under the same LC conditions, retention of tetrapeptide isomers, fixed in D-tyrosine position on CR-I (+) does not differ significantly from their corresponding LXXX enantiomer on CR-I (-) column and vice versa, demonstrating the capability of roughly estimating the retention times of the corresponding enantiomer.
By assuming, that only in case of stereoselective binding, retention times of single enantiomer on CR-I (+) and (-) columns, under the same chromatographic conditions, would differ from each other, this approach was used to study the retention behaviour of eight tetrapeptide analogues. It was concluded that N-terminal ⍰-amino group in Tyr is responsible for chiral recognition of Tyr-Arg-Phe-Lys-NH2.

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References:
[1] Upmanis T., Kažoka H., Arsenyan P. J. Chromatogr. A 2020, 1622, 461152

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