Does the edge-to-face interaction between aromatic rings occur in cyclolinopeptide A analogues?.

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Streszczenie

We measured 1H-NMR, fluorescence and CD spectra of cyclolinopeptide A (CLA), its tyrosine analogues with each or both phenylalanines substituted by tyrosine (c-[LeuIleIleLeuValProProTyrPhe], c-[LeuIleIleLeuValProProPheTyr] and c-[LeuIleIleLeuValProProTyrTyr]), and their linear counterparts with the starting sequence leu-Ile-Ile-Leu-Val-Pro-Pro-Phe-Phe (LA). It follows from CD spectra that the conformations of all cyclic peptides are similar to that of CLA; the conformations of linear peptides are more diversified, with the conformation of [Tyr9]LA being most similar to CLA. NMR studies suggest that aromatic rings in cyclic peptides are situated perpendicular to each other, manifesting edge-to-face pairing. Accordingly, the residue in position 9 is shielded ('edge'), and a residue in position 8 is the shielding one ('face'). This effect is not present in the case of linear peptides. Fluorescence quantum yields were much lower for cyclic peptides than for linear ones, indicating the interaction of closely located aromatic chromophores. Those quantum yields depend on the relative position of Tyr in the peptide chain. Another factor influenced by the position in the peptide chain is the optical activity of aromatic side chains (optically active in position 8, inactive in position 9). This phenomenon could be explained by the differences in the side-chain conformation of both aromatic residues.

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