

Phosphorylation as a method of tuning the enantiodiscrimination potency of quinine : an NMR study.

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Streszczenie

Quinines phosphorylated at the C-9 hydroxyl group (diphenyl and diethyl phosphates) were synthesized and validated as novel effective chiral solvating agents in two alternative methods based on ^1H and ^{31}P NMR spectroscopy. Tested with a representative set of racemic analytes, the title compounds induced shift nonequivalence effects in ^1H NMR signals with values up to 0.1-0.2 ppm for 3,5-dinitrobenzoyl-substituted amino acids. In terms of enantiodifferentiation extent and application range, introduction of a phosphate group was proven to be superior compared to the action of nonmodified quinine. Interestingly, a temperature decrease to reach the slow exchange conditions also produced nonequivalences in the ^{31}P NMR spectra of the selectors. Comprehensive NMR analysis showed the existence of two conformations (closed 1 and 2) for both quinines in their free forms and the open 3 arrangement for the protonated ones. The crystal structure of diethylphosphorylquinine hydrochloride dichloromethane hemisolvate revealed a similar conformation to that observed in solution. Structures of complexes of phosphorylated quinines with selected ligands were determined with the use of NMR-based molecular modeling studies.

Słowa kluczowe

alkaloids, phosphorylation, conformation analysis, chiral auxiliaries, NMR spectroscopy

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