Comparison of the acid-base properties of ribose and 2'-deoxyribose nucleotides.

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Streszczenie

The extent to which the replacement of a ribose unit by a 2′-deoxyribose unit influences the acid–base properties of nucleotides has not hitherto been determined in detail. In this study, by potentiometric pH titrations in aqueous solution, we have measured the acidity constants of the 5′-di- and 5′-triphosphates of 2′-deoxyguanosine [i.e., of $H_2(dGDP)^-$ and $H_2(dGTP)^{2-}$] as well as of the 5′-mono-, 5′-di-, and 5′-triphosphates of 2′-deoxyadenosine [i.e., of $H_2(dAMP)^{\pm}$, $H_2(dADP)^-$, and $H_2(dATP)^{2-}$]. These 12 acidity constants (of the 56 that are listed) are compared with those of the corresponding ribose derivatives (published data) measured under the same experimental conditions. The results show that all protonation sites in the 2′-deoxynucleotides are more basic than those in their ribose counterparts. The influence of the 2′-OH group is dependent on the number of 5′-phosphate groups as well as on the nature of the purine nucleobase. The basicity of N7 in guanine nucleotides is most significantly enhanced (by about 0.2 p*K* units), while the effect on the phosphate groups and the N1H or $N1H^+$ sites is less pronounced but clearly present. In addition, ^1H NMR chemical shift change studies in dependence on pD in D_2O have been carried out for the dAMP, dADP, and dATP systems, which confirmed the results from the potentiometric pH titrations and showed the nucleotides to be in their *anti* conformations. Overall, our results are not only of relevance for metal ion binding to nucleotides or nucleic acids, but also constitute an exact basis for the calculation, determination, and understanding of perturbed pK_a values in DNAzymes and ribozymes, as needed for the delineation of acid–base mechanisms in catalysis.