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A theoretical study of structures and stabilities of hexopyranose anomers in vacuo and in aqueous solution

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Hexopyranose has a stereogenic center at C1 (Fig. 1) and there are stereoisomers called anomers (α,β). In vacuo, it is supposed that α-anomer of hexose is more stable than β-anomer because of the anomeric effect [1]. In aqueous solution at room temperature, however, it is experimentally observed [2] that glucopyranose exists as a mixture of ~36% α-anomer and ~64% β-anomer, and that mannopyranose exists as a mixture of ~68% α-anomer and ~32% β-anomer. The origin of the difference has not been clarified yet. In this study, we show the solvation stabilization energies of the hexopyranose anomers in aqueous solution.

In vacuo, geometry optimization calculations were carried out at MP2/aug-cc-pVDZ. It was found that α-anomers are more stable than β-anomers and glucopyranose is more stable than mannnopyranose (Fig. 2). In aqueous solution, QM/MM-MD method was performed to calculate the stabilization energy due to solvation. The conditions of MD simulation were as follows: the number of water molecules was 148, and a time step of MD was 0.2 fs and total of 5000 steps were performed. Structures at some steps were extracted (total of 15 structures for each anomer) and were optimized. Relative energies of 60 structures are shown in Fig. 3. For glucopyranose, solvation stabilization energy of β-anomer is larger than that of α-anomer and β-anomer is more stable than α-anomer. As to mannopyranose, solvation stabilization energy of β-anomer is not large enough to make β-anomer more stable than α-anomer. These results are consistent with the experimental observation.

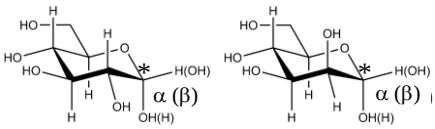

Figure 1. Structures of glucopyranose (left) and mannopyranose (right)

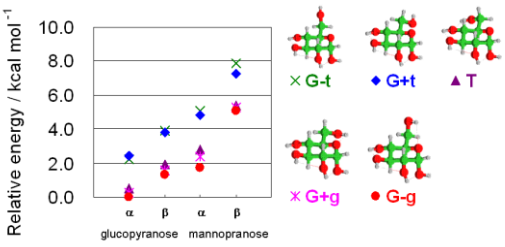

Figure 2. Relative energies of anomers in vacuo

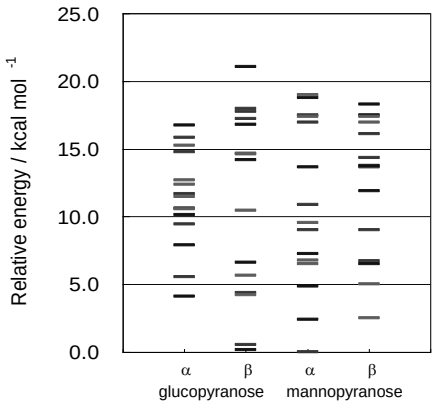

Figure 3. Relative energies of anomers in aqueous solution

Ref: [1] U. Salzner, P.R. Schleyer, *J. Org. Chem*., **59**, 2138-2155 (1994).

[2] S. J. Angyal, *Angew. Chem. Int. Ed. Engl.*, **8**, 157-166 (1969).