Rotational Spectrum and Conformational Preferences of the 6-Carbon Cetose Sugar of Fructose

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Last year we reported the rotational spectrum of the pentose sugar ribose [1]. The molecule exhibits a large conformational variety, with six conformers confined within a small energy window of ca. 4.6 kJ mol^{-1}. In all cases a six-membered pyranose form was found, with β-anomers sligthly more stable and a distribution of both $^{1}C_4$ and $^{4}C_1$ rings.

In order to check how the conformational equilibrium is affected by the introduction of an additional carbon atom and a cetose group we now report the rotational spectrum of fructose [2]. Similarly to the previous study the sample was vaporized using a ps Nd-YAG laser and probed in a supersonic expansion with a Balle-Flygare-type Fourier-transform microwave spectrometer.

The rotational spectrum revealed that fructose is essentially locked around a most stable pyranose conformation with a $^{2}C_5$ ring configuration (equivalent to $^{1}C_4$ in aldoses). The structure of the molecule was derived from the rotational constants of the parent and seven additional ^{13}C and D isotopologues, some of them measured in natural abundance. The enhanced stability of the observed conformation is attributed to a cooperative network of five O-H···O intramolecular hydrogen bonds. Exo and endo anomeric effects are consistent with the observed structure. A comparison with ribose and deoxyribose will also be presented.

Figure 1. Intramolecular hydrogen bonds (red dots, angström) in the most stable conformation of fructose (cc-β-pyr-$^{2}C_5$-G+G-, left) and comparison between the experimental carbon skeleton (inner blue spheres) and the best matching ab initio structure (right).

[1] E. J. Cocinero, A. Lesarri, P. Écija, F. J. Basterretxea, J.-U. Grabow, J. A. Fernández, F. Castaño, *Angew. Chem. Int. Ed.*, **2012**, *51*, 3119.
[2] E. J. Cocinero, A. Lesarri, P. Écija, A. Cimas, B. G. Davis, F. J. Basterretxea, J. A. Fernández, F. Castaño, *J. Am. Chem. Soc.*, **2013**, *135*, 2845.