The conformational behavior of ketohexoses D-Fructose, L-Sorbose, D-Tagatose and D-Psicose has been revealed from their rotational spectra. A broadband microwave spectrometer (CP-FTMW)\(^a\) combined with a laser ablation (LA) source\(^b\) has been used to rapidly acquire the rotational spectra in the 6 to 12 GHz frequency range. All observed species are stabilized by complicated intramolecular hydrogen-bonding networks. Structural motifs related to the sweetness of ketohexoses are revealed.