Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Acyclic forms of aldohexoses and ketohexoses in aqueous and DMSO solutions: conformational features studied by molecular dynamics simulations

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Tab. S1. The $\Delta F_{P\text{-}F}$ values (in [kJ/mol]) calculated for the studied compounds in the presence of explicit solvent (water or DMSO). Due to large degree of arbitrariness in the definition of the *P* and *F* regions (see *Methods* section in the main manuscript), several different combinations of the *a* and *b* values (in [nm]) are considered.

	water			DMSO		
	$a = 0.25$, $b = 0.3$	$a = 0.3$, $b = 0.2$	$a = 0.35$, $b = 0.35$	$a = 0.25$, $b = 0.3$	$a = 0.3$, $b = 0.2$	$a = 0.35$, $b = 0.35$
aldohexoses						
D-All	30.8	36.4	18.0	33.7	39.1	19.8
D-Alt	29.5	29.2	17.5	30.9	27.5	18.2
D-Glc	30.6	36.8	17.7	32.7	42.4	20.9
D-Man	29.5	34.3	16.1	29.5	28.6	18.5
D-Gul	30.8	36.2	17.8	25.8	30.3	14.6
D-Ido	28.2	43.8	13.5	30.4	45.7	16.3
D-Gal	29.1	37.9	15.6	28.9	30.3	15.6
D-Tal	30.7	36.1	17.9	30.6	39.9	16.4
ketohexoses						
D-Fru	28.4	32.4	17.9	25.5	30.7	19.1
D-Psi	27.5	36.4	16.7	22.8	28.1	18.3
D-Sor	27.4	36.8	16.3	25.8	35.5	19.7
L-Sor	27.2	36.7	16.4	25.7	33.1	19.0
D-Tag	26.7	32.3	16.8	25.0	24.4	18.4

Tab. S2. The occurrences (in [number of HBs/timeframe]) of intramolecular hydrogen bonds and their estimated lifetimes. The data correspond to the unbiased MD simulations of aldo- and ketohexoses in explicit water. The 'pyranose' and 'furanose' labels correspond to HBs between aldehyde or ketone moieties with the hydroxyl groups that may hypothetically contribute in the formation of pyranose and furanose rings, respectively.

	pyranose		furanose		total	
	occurrence	lifetime [ps]	occurrence	lifetime [ps]	occurrence	lifetime [ps]
D-All	0	-	0.001	6.53	1.44	187
D-Alt	0	-	0	-	1.02	390
D-Glc	0	-	0.002	7.8	0.92	1101
D-Man	0	-	0	-	0.52	302
D-Gul	0	-	0	-	0.50	599
D-Ido	0	-	0.002	6.6	0.56	458
D-Gal	0	-	0	-	0.27	1759
D-Tal	0	-	0	-	0.73	361
ketohexoses						
D-Fru	0	-	0	-	0.36	153
D-Psi	0	-	0.001	7.7	0.57	415
D-Sor	0	-	0.01	218	0.57	548
L-Sor	0	-	0.000	134	0.57	512
D-Tag	0	-	0.001	7.6	0.21	5532

Tab. S3. The occurrences (in [number of HBs/timeframe]) of intramolecular hydrogen bonds and their estimated lifetimes. The data correspond to the unbiased MD simulations of aldo- and ketohexoses in explicit DMSO solvent. Other details as in Tab. S1.

	pyranose		furanose		total	
	occurrence	lifetime [ps]	occurrence	lifetime [ps]	occurrence	lifetime [ps]
D-All	0	-	0	-	2.18	220
D-Alt	**0**	-	0	-	1.61	411
D-Glc	0	-	0.002	18.0	1.46	1382
D-Man	0	-	0	-	1.16	652
D-Gul	0	-	0.001	7.4	0.82	705
D-Ido	0	-	0.003	16.5	1.17	910
D-Gal	0	-	0	-	1.06	1124
D-Tal	0	-	0	-	1.16	404
ketohexoses						
D-Fru	0	-	0.001	16.6	0.91	305
D-Psi	0	-	0.001	14.6	0.68	1034
D-Sor	0	-	0.017	533.4	0.91	290
L-Sor	0	-	0.016	543.4	0.89	337
D-Tag	0	-	0.002	156.0	0.64	2180

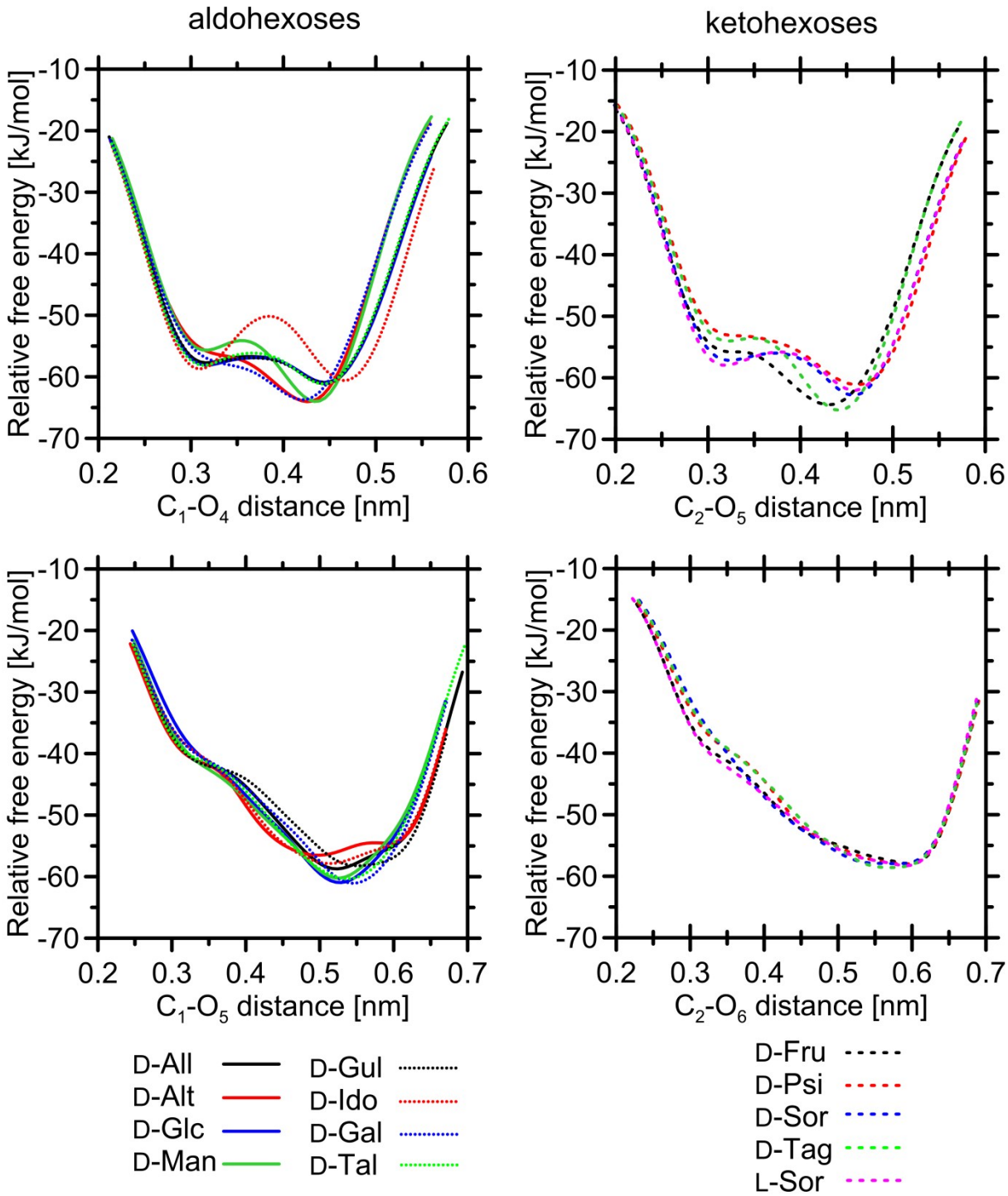

Fig. S1. One dimensional free energy profiles calculated for the selected interatomic distances of aldo- (left panels) and ketohexose (right panels) molecules. All plots correspond to the enhanced-sampling MD simulations in the explicit water solvent. See the main manuscript for details.

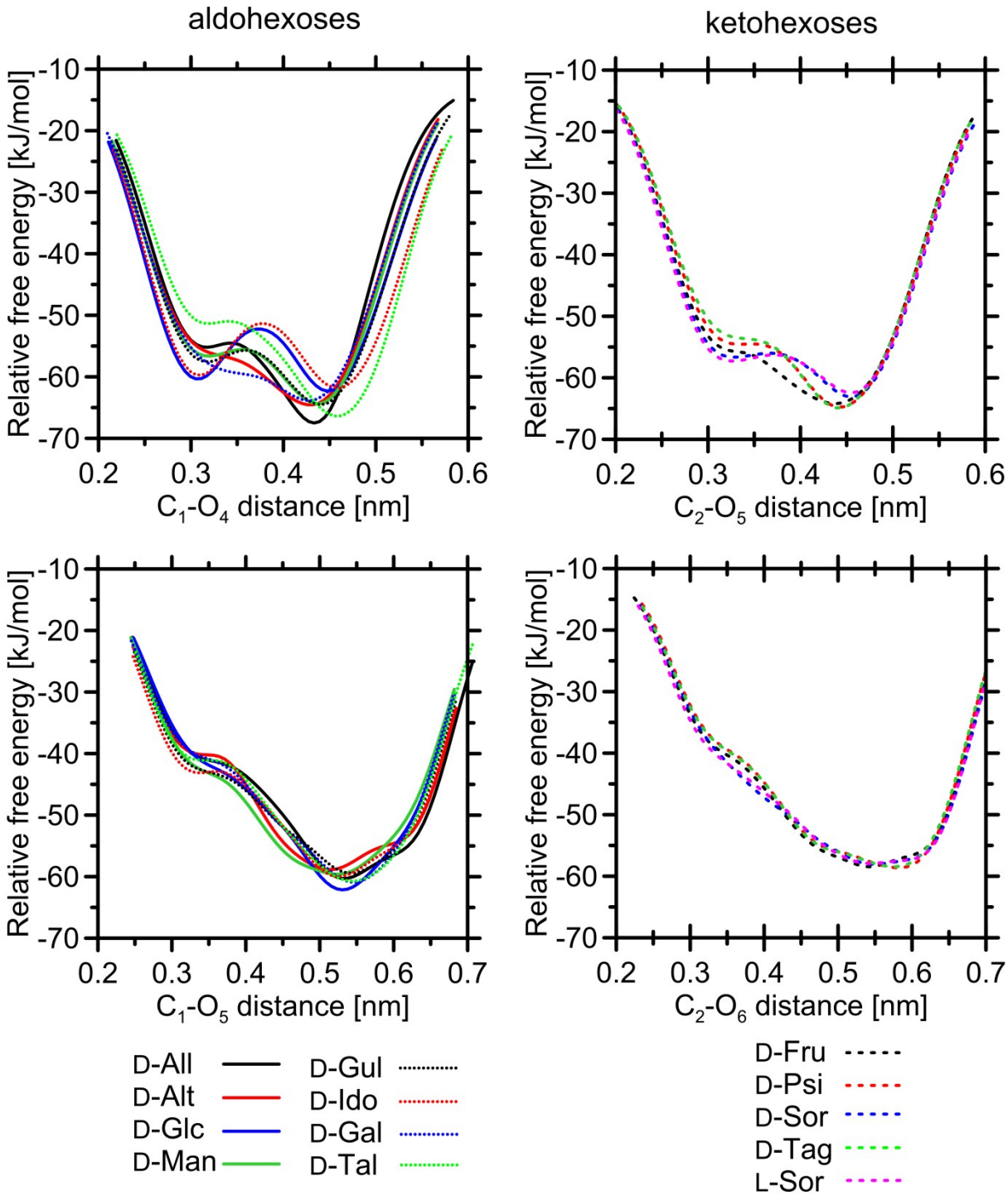

Fig. S2. One dimensional free energy profiles calculated for the selected interatomic distances of aldo- (left panels) and ketohexose (right panels) molecules. All plots correspond to the enhanced-sampling MD simulations in the explicit DMSO solvent. See the main manuscript for details.

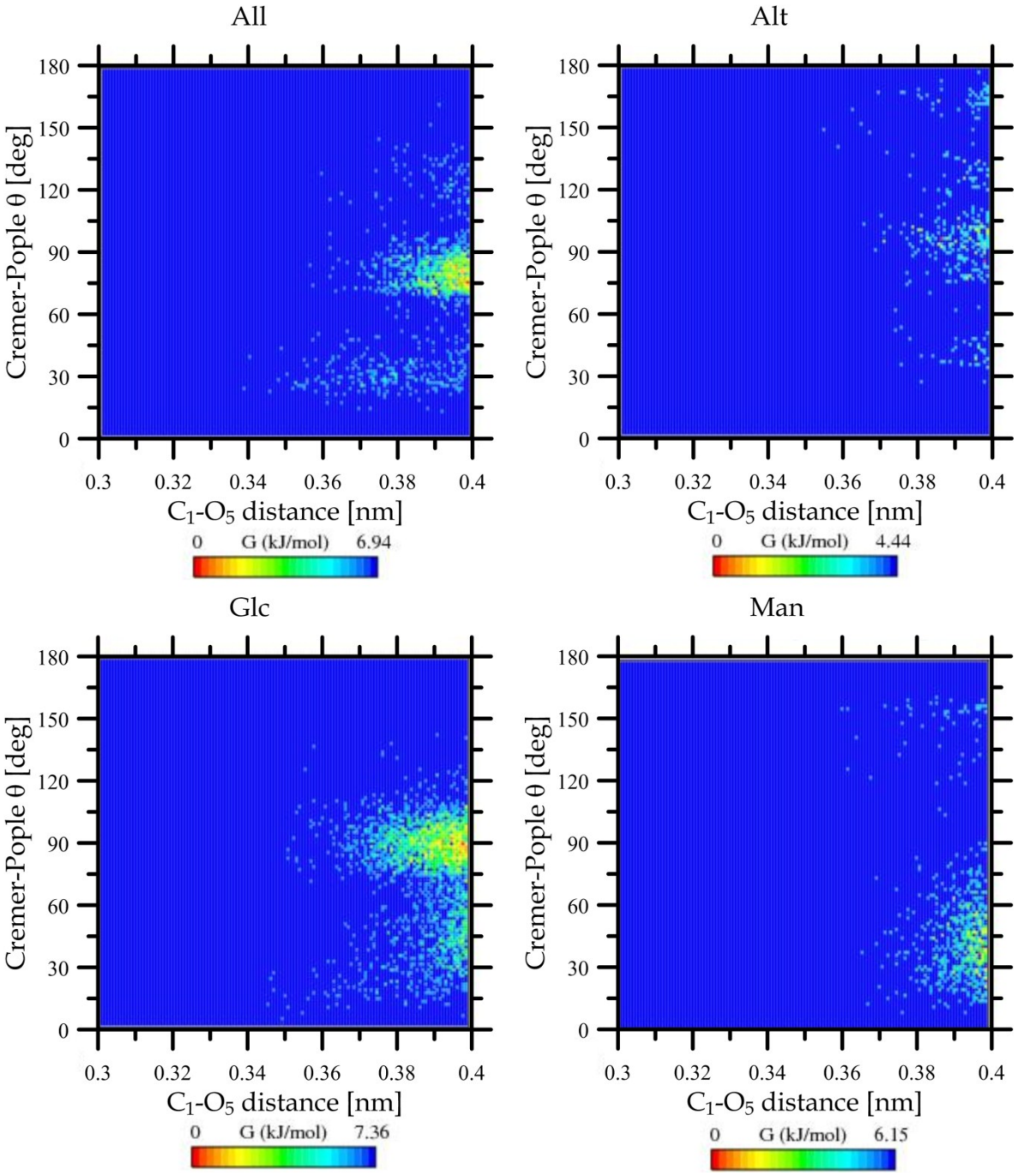

Fig. S3. Two dimensional θ vs. d_1 free energy maps calculated for four aldohexoses of the D-series (All, Alt, Glc and Man). θ is the Cremer-Pople parameter describing the geometry of the ring created by the following six atoms: C_1, C_2, C_3, C_4, C_5 and O_5 whereas d_1 is the interatomic O_5-C_1 distance. All plots correspond to the unbiased MD simulations in the explicit water solvent. See the main manuscript for details.

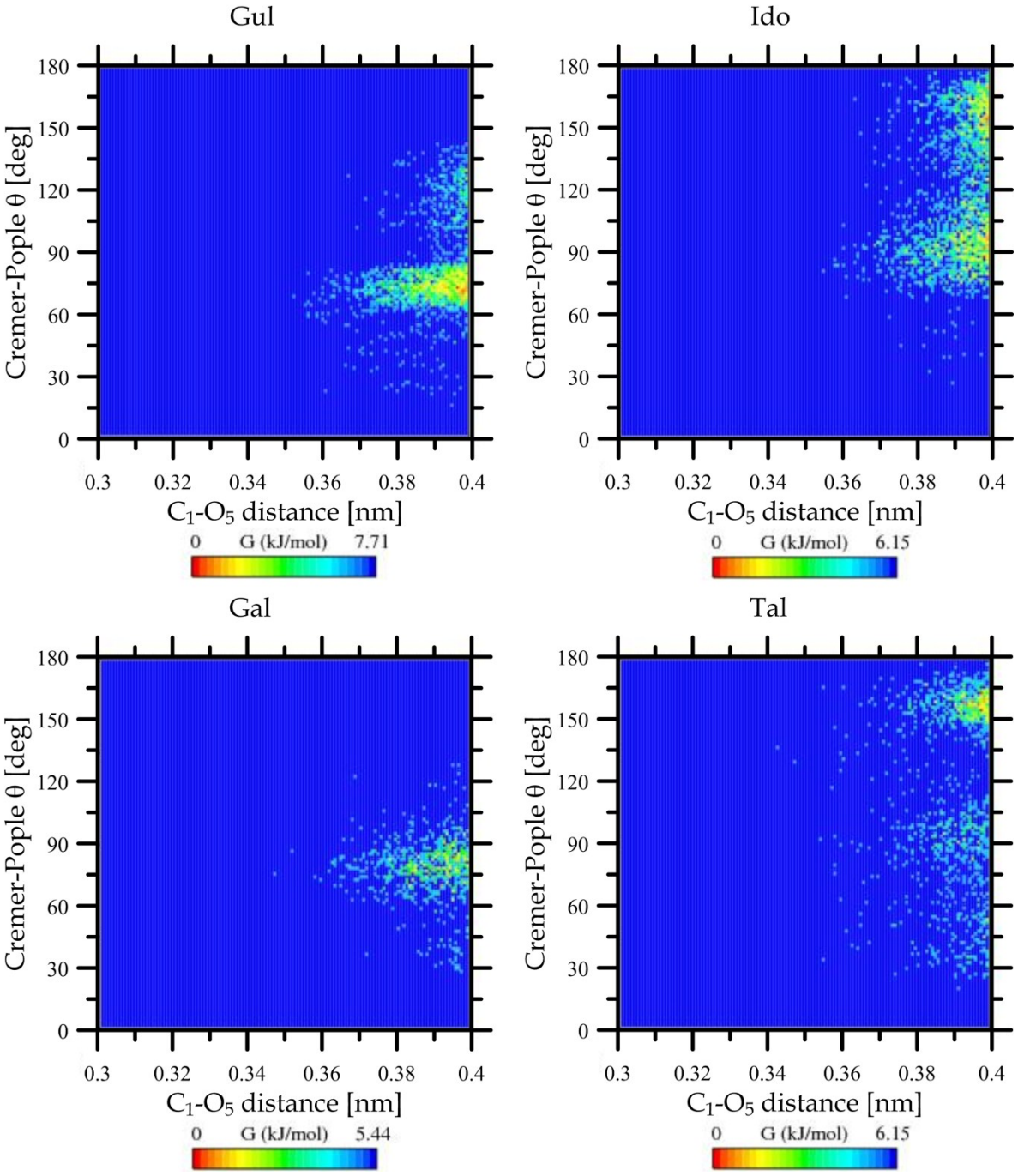

Fig. S4. Two dimensional θ vs. d_1 free energy maps calculated for four aldohexoses of the D-series (Gul, Ido, Gal and Tal). θ is the Cremer-Pople parameter describing the geometry of the ring created by the following six atoms: C_1, C_2, C_3, C_4, C_5 and O_5 whereas d_1 is the interatomic O_5-C_1 distance. All plots correspond to the unbiased MD simulations in the explicit water solvent. See the main manuscript for details.