Supporting Information for

Studies of arabinose and mannose related anionic species, and comparison to ribose and fructose

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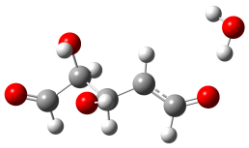
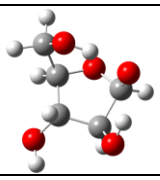
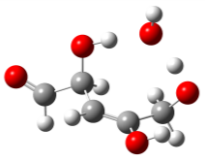
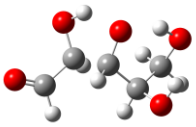
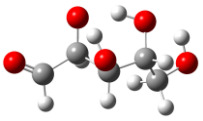
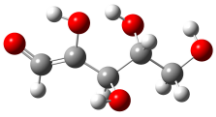
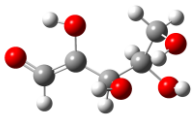
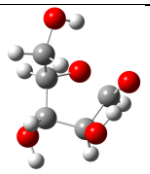
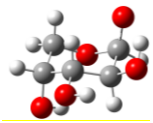
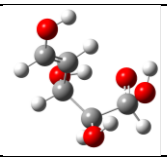
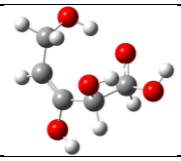
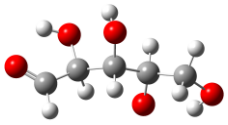
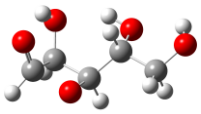
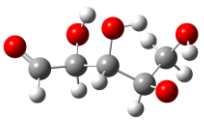
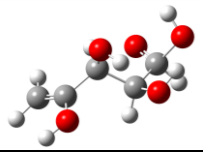
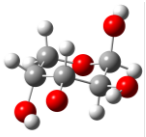
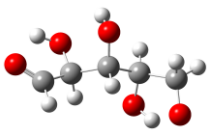
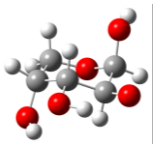
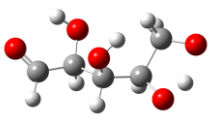
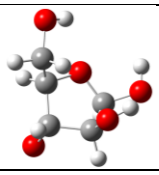
More low energy isomers of (arabinose-H)$^-$, (arabinose-H_2O)$^-$, (mannose-H)$^-$, and (mannose-H_2O)$^-$ anions are summarized in Figures S5 to S6, and S8 to S9 in the Supporting Information. Note that the figure numbers in the S.I. document are related to those of the text figures, as for example Figure S5 ⇔ Figure 5.

Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (5C)H	β-furanose – (1)H	open chain (A) – (4C)H	open chain (A) – (3)H
ΔE (eV)	0.00	0.39	0.40	0.45
VDE (eV)	**3.52**	**3.82**	**4.51**	**4.07**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (2)H	open chain (B) – (2C)H	open chain (A) – (2C)H	β-furanose – (1)H
ΔE (eV)	0.52	0.53	0.56	0.63
VDE (eV)	**3.96**	**2.62**	**2.50**	**3.92**
Optimized Anionic structure				
Structural Polymorphism	β-pyranose – (1)H	β-furanose – (5C)H	β-furanose – (3C)H	open chain (B) – (4)H
ΔE (eV)	0.65	0.70	0.74	0.85
VDE (eV)	**3.50**	**3.55**	**3.67**	**3.31**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (3)H	open chain (A) – (4)H	β-pyranose – (4C)H	β-pyranose – (3)H
ΔE (eV)	0.96	0.97	0.98	0.98
VDE (eV)	**4.01**	**3.47**	**3.35**	**3.13**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (5)H	β-pyranose – (2)H	open chain (A) – (5)H	β-furanose – (3)H
ΔE (eV)	1.04	1.21	1.24	1.39
VDE (eV)	**3.17**	**2.83**	**3.19**	**2.77**

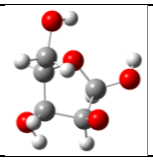
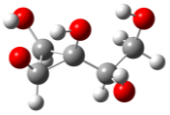
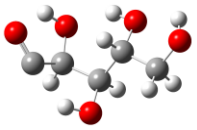
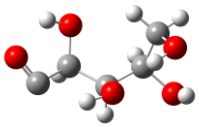
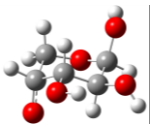
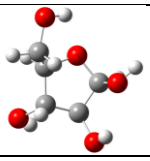
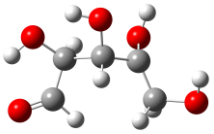
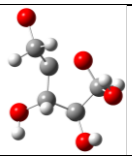
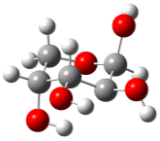
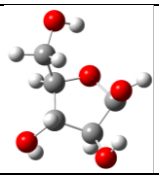
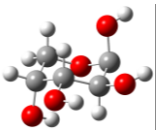
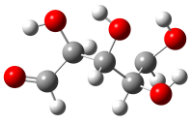
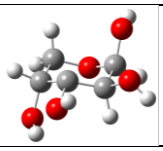
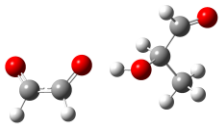
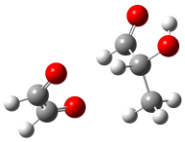
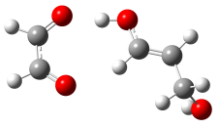
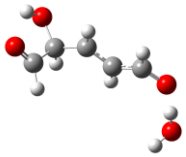
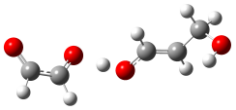
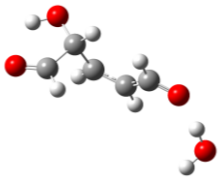
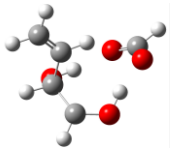
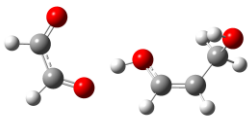
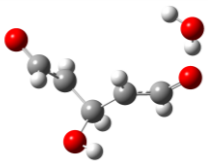
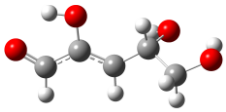
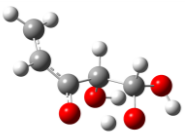
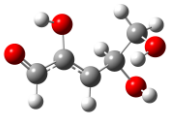
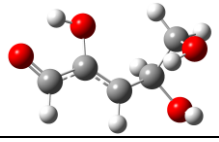
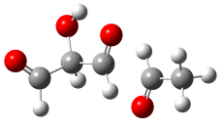
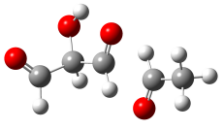
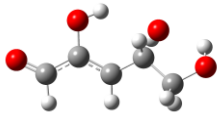
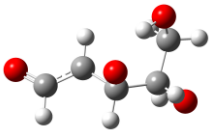
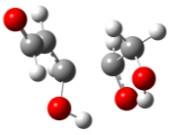
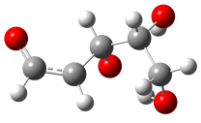
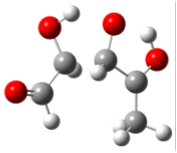
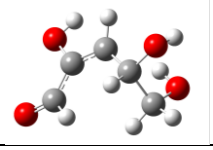
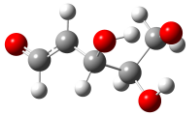
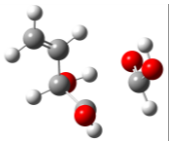
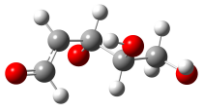
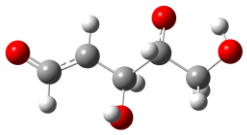
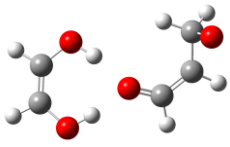
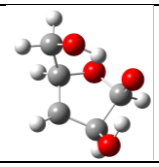
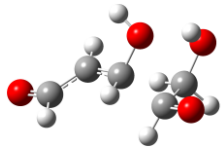
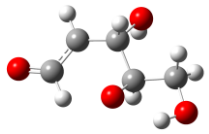
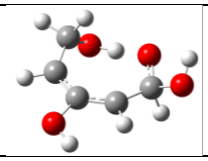
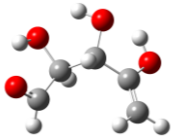
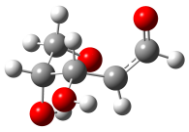
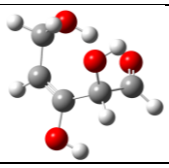
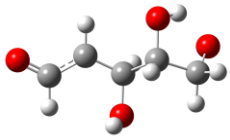
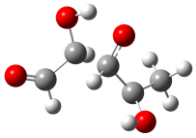
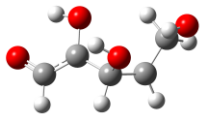
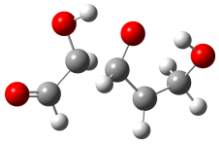
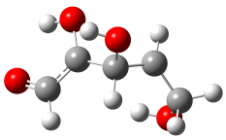
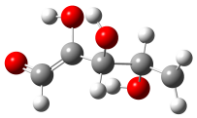
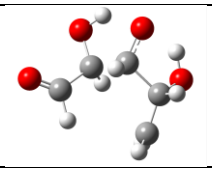
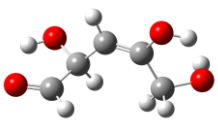
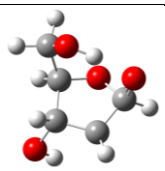
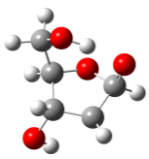
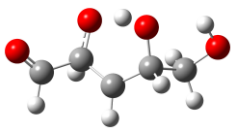
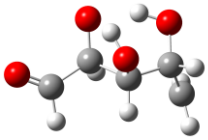
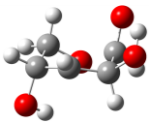
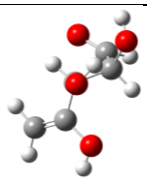
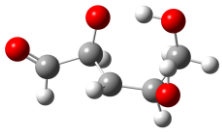
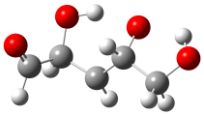
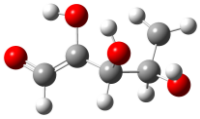
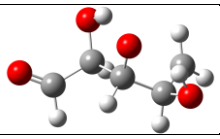
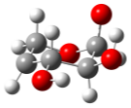
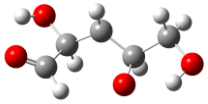
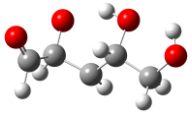
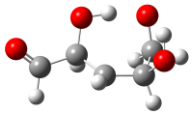
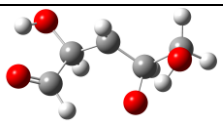
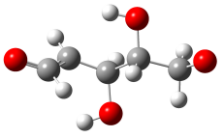
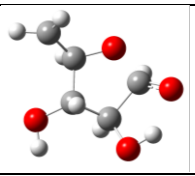
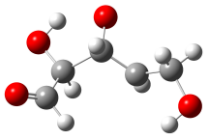
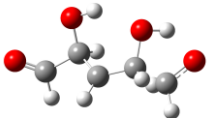
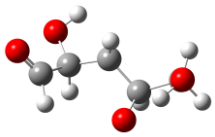
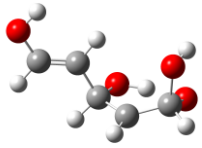
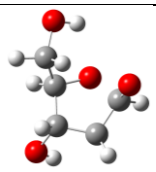
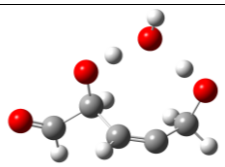
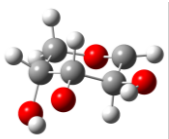
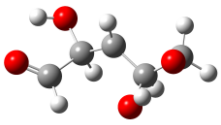
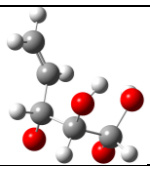
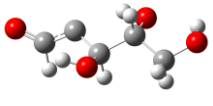
Optimized Anionic structure				
Structural Polymorphism	β-furanose – (2)H	open chain (A) – (3C)H	open chain (B) – (1C)H	open chain (A) – (1C)H
ΔE (eV)	1.50	1.51	1.14	1.74
VDE (eV)	**2.83**	**3.67**	**2.56**	**2.35**
Optimized Anionic structure				
Structural Polymorphism	β-pyranose – (4)H	β-furanose – (2C)H	open chain (B) – (4C)H	β-furanose – (4C)H
ΔE (eV)	1.38	2.25	2.29	2.44
VDE (eV)	**2.42**	**1.80**	**1.74**	**1.74**
Optimized Anionic structure				
Structural Polymorphism	β-pyranose – (2C)H	β-furanose – (1C)H	β-pyranose – (1C)H	open chain (A) – (5C)H
ΔE (eV)	2.44	2.58	2.63	2.69
VDE (eV)	**1.97**	**2.14**	**1.92**	**1.57**
Optimized Anionic structure				
Structural Polymorphism	β-pyranose – (3C)H			
ΔE (eV)	2.79			
VDE (eV)	**1.22**			

Figure S5 Optimized geometries of the typical low energy anionic isomers of (arabinose – H)$^-$ based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The structural presentation is the same as those in the main text Figures 4-9. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (2)H – (5)OH	open chain (A) – (2)H – (5)OH	open chain (B) – (2)H – (4)OH	open chain (B) – (5C)H – (3)OH
ΔE (eV)	0.00	0.13	0.21	0.22
VDE (eV)	**2.90**	**2.63**	**3.06**	**1.95**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (2)H – (4)OH	open chain (B) – (5C)H – (3)OH	β-furanose – (1)H – (5)OH	open chain (A) – (2)H – (4)OH
ΔE (eV)	0.25	0.30	0.30	0.33
VDE (eV)	**3.15**	**1.97**	**2.87**	**2.98**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (5C)H – (2)OH	open chain (B) – (2C)H – (3)OH	β-furanose – (3C)H – (5)OH	open chain (A) – (2C)H – (3)OH
ΔE (eV)	0.49	0.68	0.76	0.91
VDE (eV)	**3.80**	**1.50**	**1.56**	**1.36**
Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (2C)H – (3)OH)	open chain (A) – (3)H – (5)OH	open chain (B)– (3)H – (5)OH	open chain (B)– (2C)H – (3)OH
ΔE (eV)	0.91	1.04	1.04	1.06
VDE (eV)	**1.36**	**1.74**	**1.74**	**1.38**
Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (3)H – (2)OH	open chain (A) – (4)H – (2)OH	open chain (A) – (3)H – (2)OH	open chain (A) – (4C)H – (5)OH
ΔE (eV)	1.20	1.25	1.29	1.36
VDE (eV)	**4.09**	**3.54**	**4.03**	**2.32**
Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (2C)H – (3)OH	open chain (A) – (5)H – (2)OH	β-furanose – (2)H – (5)OH	open chain (B) – (3)H – (2)OH

ΔE (eV)	1.39	1.41	1.43	1.47
VDE (eV)	**1.47**	**4.25**	**1.57**	**3.77**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (4)H – (2)OH	open chain (A) – (3)H – (4)OH	β-furanose – (1)H – (3)OH	open chain (A) – (3)H – (2)OH
ΔE (eV)	1.56	1.57	1.59	1.61
VDE (eV)	**3.94**	**3.96**	**3.55**	**3.57**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (4)H – (2)OH	β-furanose – (3C)H – (2)OH	open chain (B) – (4C)H – (5)OH	β-pyranose – (1)H – (2)OH
ΔE (eV)	1.62	1.63	1.63	1.64
VDE (eV)	**4.05**	**3.41**	**1.09**	**3.36**
Optimized Anionic structure				
Structural Polymorphism	β-furanose – (3C)H – (1)OH	open chain (B) – (5)H – (2)OH	open chain (B) – (4C)H – (5)OH	open chain (A) – (2C)H – (4)OH
ΔE (eV)	1.70	1.73	1.74	1.75
VDE (eV)	**1.39**	**3.95**	**2.67**	**2.67**
Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (3)H – (4)OH	open chain (B) – (2C)H – (4)OH	open chain (B) – (2C)H – (5)OH	open chain (A) – (3)H – (5)OH
ΔE (eV)	1.76	1.77	1.77	1.82
VDE (eV)	**3.41**	**2.63**	**2.89**	**3.62**
Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (4C)H – (3)OH	β-furanose – (1)H – (2)OH	β-furanose – (1)H – (2)OH	open chain (B) – (2)H – (3)OH
ΔE (eV)	1.83	1.85	1.86	1.89
VDE (eV)	**0.41**	**3.40**	**3.39**	**3.21**

Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (2)H – (5)OH	β-pyranose – (1)H – (3)OH	β-pyranose – (4C)H – (1)OH	open chain (A) – (2)H – (3)OH
ΔE (eV)	1.92	1.92	1.92	1.93
VDE (eV)	**3.97**	**3.20**	**0.83**	**3.28**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (4)H – (3)OH	open chain (A) – (2)H – (5)OH	open chain (A) – (3)H – (5)OH	β-pyranose – (1)H – (4)OH
ΔE (eV)	1.93	1.94	1.96	1.97
VDE (eV)	**3.53**	**3.01**	**4.13**	**3.17**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (4)H – (3)OH	open chain (B) – (2)H – (3)OH	open chain (A) – (5)H – (3)OH	open chain (A) – (4)H – (3)OH
ΔE (eV)	1.97	1.97	1.99	2.00
VDE (eV)	**3.20**	**3.56**	**3.97**	**3.10**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (5)H – (2)OH	β-furanose – (1)H – (5)OH	open chain (B) – (3)H – (4)OH	open chain (B) – (5)H – (3)OH
ΔE (eV)	2.03	2.03	2.06	2.06
VDE (eV)	**4.49**	**3.95**	**3.48**	**3.17**
Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (4)H – (3)OH	β-furanose – (5C)H – (2)OH	β-furanose – (1)H – (2)OH	open chain (A) – (4C)H – (3/4)OH
ΔE (eV)	2.10	2.11	2.15	2.21
VDE (eV)	**3.26**	**3.24**	**3.19**	**3.89**
Optimized Anionic structure				
Structural Polymorphism	β-pyranose – (3)H – (1)OH	open chain (B) – (5)H – (3)OH	β-furanose – (3)H – (5)OH	open chain (B) – (2C)H – (2)OH
ΔE (eV)	2.22	2.23	2.23	2.26

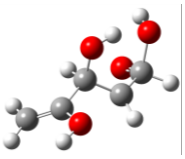
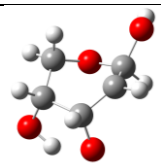
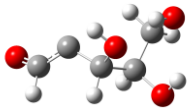
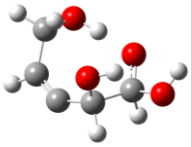
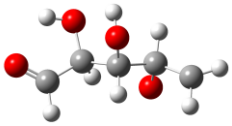
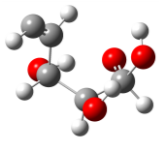
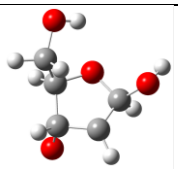
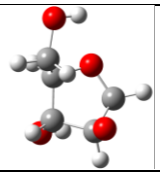
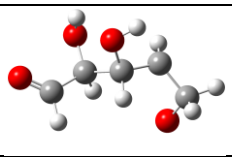
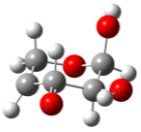
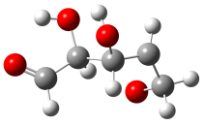
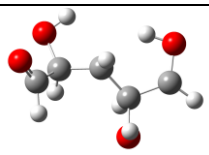
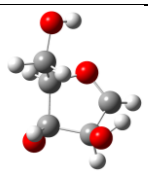
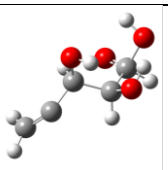
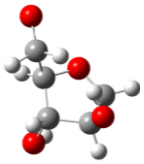
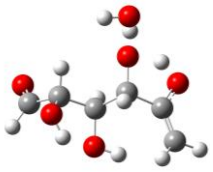
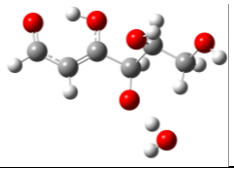
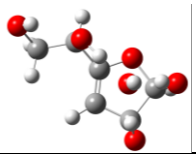
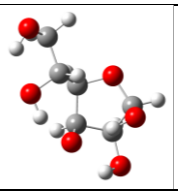
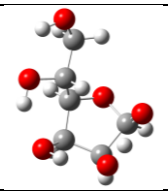
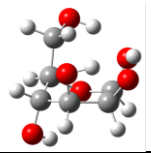
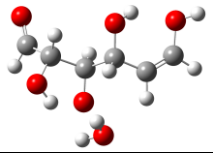
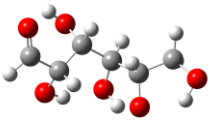
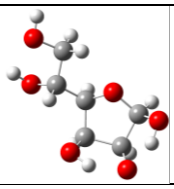
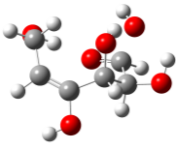
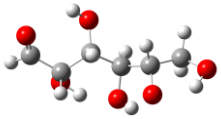
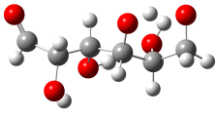
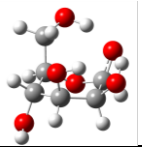
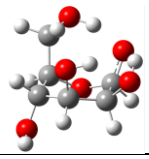
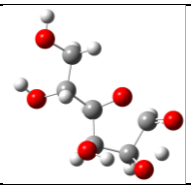
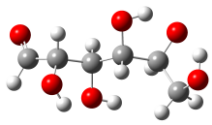
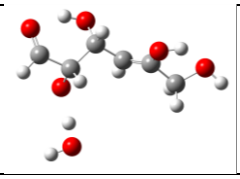
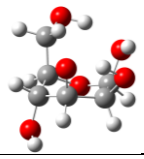
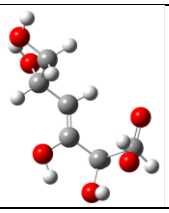
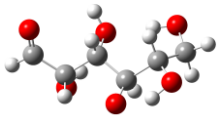
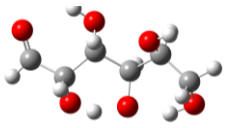
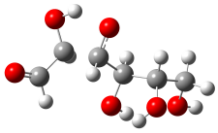
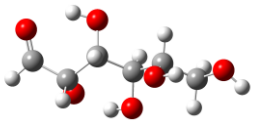
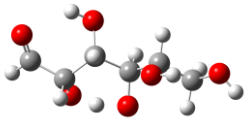
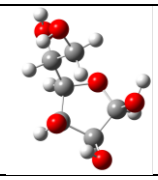
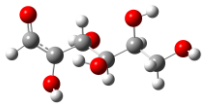
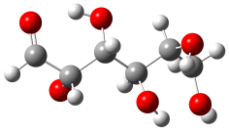
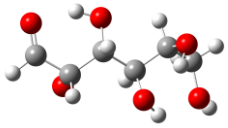
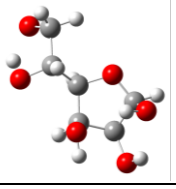
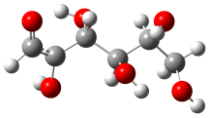
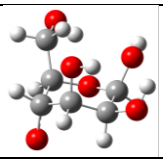
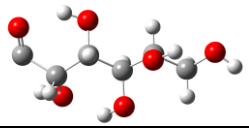
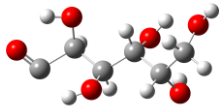
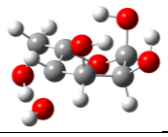
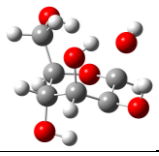
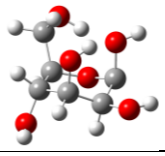
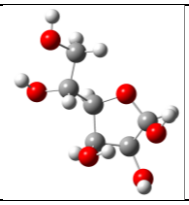
VDE (eV)	**2.93**	**3.48**	**3.73**	**3.56**
Optimized Anionic structure				
Structural Polymorphism	β-pyranose – (4C)H – (2)OH	β-pyranose – (3)H – (2)OH	open chain (A) – (2C)H – (2)OH	β-furanose – (3C)H – (3)OH
ΔE (eV)	2.27	2.29	2.35	2.42
VDE (eV)	**3.26**	**3.03**	**3.27**	**3.62**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (4)H – (5)OH	β-furanose – (5C)H – (5)OH	β-furanose– (3)H – (2)OH	β-furanose – (2)H – (1)OH
ΔE (eV)	2.44	2.53	2.53	2.54
VDE (eV)	**2.87**	**4.37**	**2.77**	**2.35**
Optimized Anionic structure				
Structural Polymorphism	open chain (B) – (5)H – (4)OH	β-pyranose – (3)H – (4)OH	open chain (B) – (3)H – (4)OH	open chain (A) – (5C)H – (3)OH
ΔE (eV)	2.55	2.57	2.61	2.64
VDE (eV)	**2.83**	**2.69**	**2.74**	**2.88**
Optimized Anionic structure				
Structural Polymorphism	β-furanose – (3)H – (1)OH	β-pyranose – (4C)H – (4)OH	β-furanose – (5)H – (1)OH	
ΔE (eV)	2.66	2.67	2.83	
VDE (eV)	**2.80**	**3.83**	**2.92**	

Figure S6 Optimized geometries of the typical low energy anionic isomers of (arabinose – H_2O)$^-$ based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The structural presentation is the same as those in the main text Figures 4-9. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure				
Structural Polymorphism	Open chian (A) – (5C)H	Open chian (B) – (3C)H	β-D-furanose – (4C)H	β-D-furanose – (3)H
ΔE (eV)	0.00	0.05	0.21	0.25
VDE (eV)	**4.32**	**3.84**	**4.43**	**4.28**
Optimized Anionic structure				
Structural Polymorphism	β-D-furanose – (1)H	β-D-pyranose – (2)H	Open chian (A) – (6C)H	Open chian (B) – (5)H
ΔE (eV)	0.38	0.56	0.58	0.63
VDE (eV)	**4.24**	**4.25**	**3.85**	**4.05**
Optimized Anionic structure				
Structural Polymorphism	β-D-furanose – (2)H	β-D-pyranose – (4C)H	Open chian (B) – (5)H	Open chian (A) – (6)H
ΔE (eV)	0.65	0.66	0.69	0.70
VDE (eV)	**3.96**	**3.76**	**3.94**	**3.85**
Optimized Anionic structure				
Structural Polymorphism	β-D-pyranose – (1)H	β-D-pyranose – (1)H	β-D-furanose – (1)H	Open chian (A) – (5)H
ΔE (eV)	0.70	0.71	0.71	0.72
VDE (eV)	**4.05**	**4.05**	**4.02**	**4.17**
Optimized Anionic structure				
Structural Polymorphism	Open chian (B) – (4C)H	β-D-pyranose – (3)H	Open chian (B) – (2)H	Open chian (B) – (3)H
ΔE (eV)	0.82	0.83	0.83	0.85
VDE (eV)	**3.70**	**3.90**	**3.76**	**3.48**

Optimized Anionic structure				
Structural Polymorphism	β-D-furanose – (3C)H	Open chian (A) – (4)H	Open chian (B) – (4)H	Open chian (A) – (3)H
ΔE (eV)	0.87	0.88	0.90	0.97
VDE (eV)	**3.50**	**3.57**	**4.02**	**3.55**
Optimized Anionic structure				
Structural Polymorphism	Open chian (B) – (2)H	Open chian (B) – (3)H	β-D-furanose – (3)H	Open chian (B) – (2C)H
ΔE (eV)	1.00	1.04	1.14	1.16
VDE (eV)	**3.65**	**3.67**	**3.35**	**2.71**
Optimized Anionic structure				
Structural Polymorphism	Open chian (A) – (2)H	Open chian (A) – (2)H	β-D-furanose – (6)H	Open chian (A) – (2C)H
ΔE (eV)	1.26	1.26	1.31	1.35
VDE (eV)	**3.15**	**3.15**	**2.95**	**2.30**
Optimized Anionic structure				
Structural Polymorphism	β-D-pyranose – (4)H	Open chian (A) – (3C)H	Open chian (B) – (1C)H	Open chian (A) – (1C)H
ΔE (eV)	1.61	1.96	2.11	2.13
VDE (eV)	**2.73**	**3.05**	**2.10**	**1.99**
Optimized Anionic structure				
Structural Polymorphism	β-D-pyranose – (5C)H	β-D-pyranose – (2C)H	β-D-pyranose – (1C)H	β-D-furanose – (2C)H
ΔE (eV)	2.13	2.18	2.63	2.64
VDE (eV)	**2.31**	**2.31**	**2.26**	**1.64**

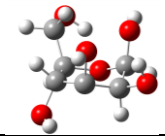
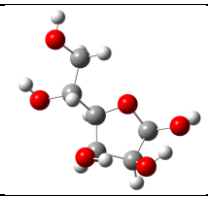
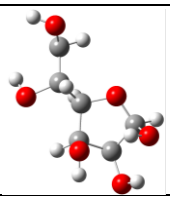
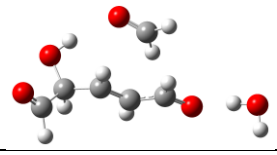
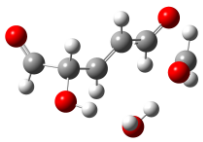
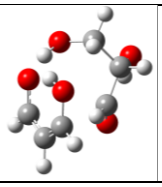
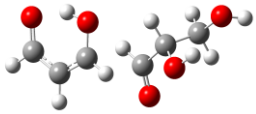
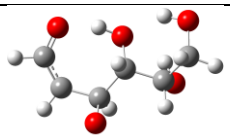
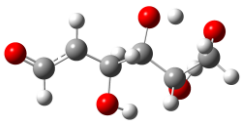
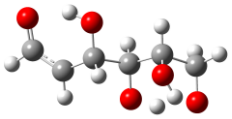
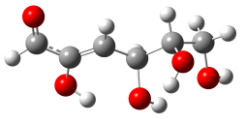
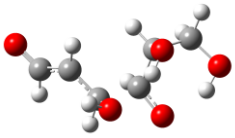
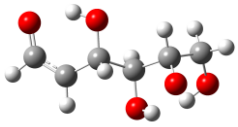
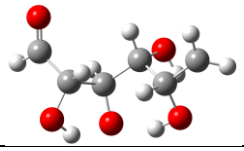
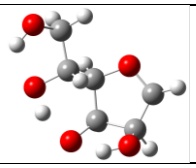
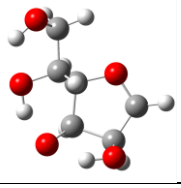
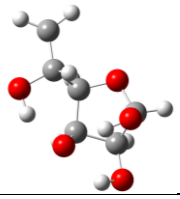
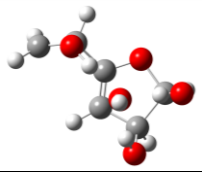
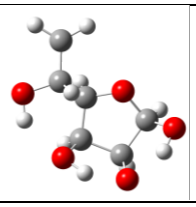
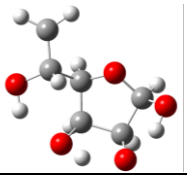
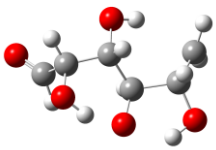
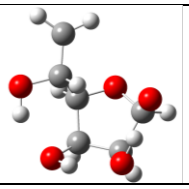
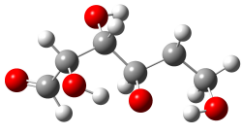
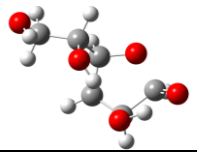
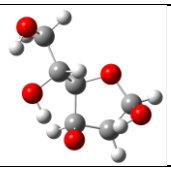
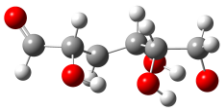
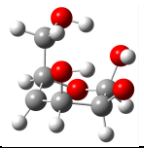
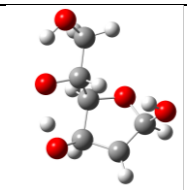
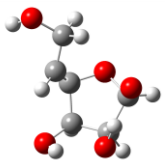
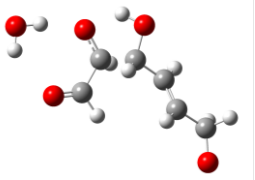
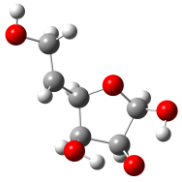
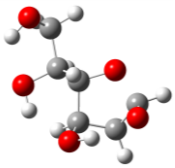
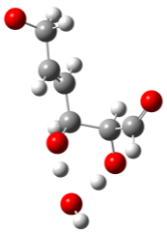
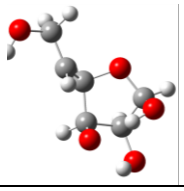
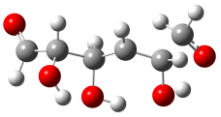
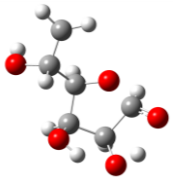
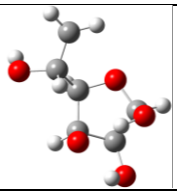
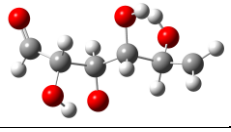
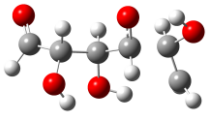
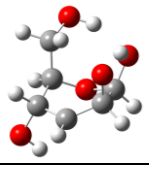
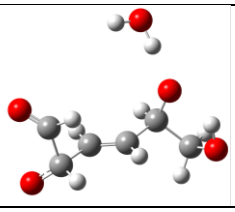
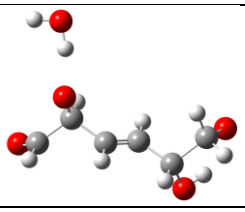
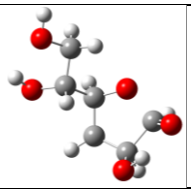
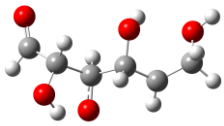
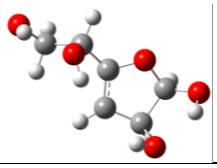
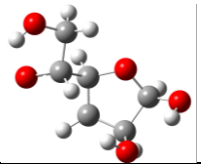
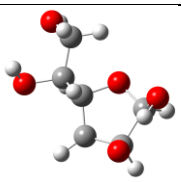
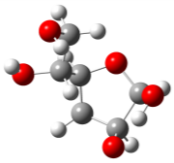
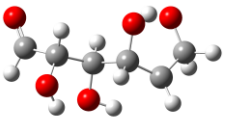
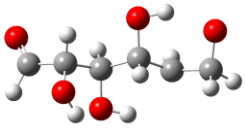
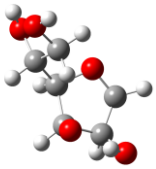
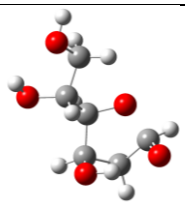
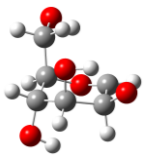
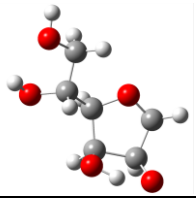
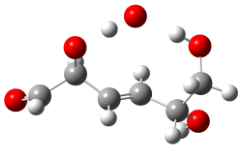
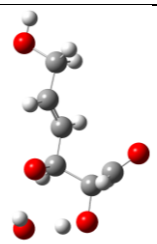
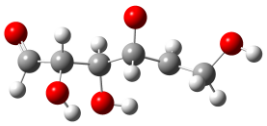
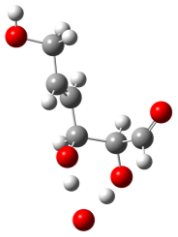
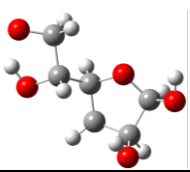
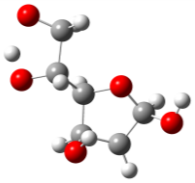
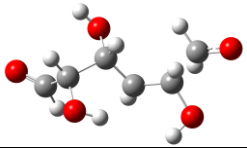
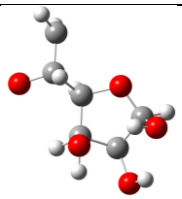
Optimized Anionic structure				
Structural Polymorphism	β-D-pyranose – (3C)H	β-D-furanose – (1C)H	β-D-furanose – (6C)H	
ΔE (eV)	2.70	2.80	2.83	
VDE (eV)	**1.83**	**1.79**	**1.57**	

Figure S8 Optimized geometries of the typical low energy anionic isomers of (mannose – H)$^-$ based on B3LYP/6-311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The structural presentation is the same as those in the main text Figures 4-9. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.

Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (6)H – (4)OH	open chain (A) – (6)H – (4)OH	open chain (A) – (4)H – (2)OH	open chain (B) – (4)H – (2)OH
ΔE (eV)	0.00	0.03	0.03	0.64
VDE (eV)	**2.30**	**1.91**	**1.50**	**1.11**
Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (3)H – (2)OH	open chain (A) – (6)H – (2)OH	open chain (A) – (6)H – (2)OH	open chain (A) – (2C)H – (3)OH
ΔE (eV)	0.68	0.68	0.70	0.71
VDE (eV)	**4.09**	**4.30**	**4.10**	**0.87**
Optimized Anionic structure				
Structural Polymorphism	open chain (C) – (4)H – (2)OH	open chain (A) – (5)H – (2)OH	open chain (A) – (3)H – (6)OH	β–D–furanose – (3)H – (1)OH
ΔE (eV)	0.75	0.82	0.91	0.97
VDE (eV)	**3.90**	**4.10**	**4.19**	**3.32**
Optimized Anionic structure				
Structural Polymorphism	β–D–furanose– (3)H – (1)OH	β–D–furanose– (3)H – (6)OH	β–D–furanose– (4C)H – (6)OH	β–D–furanose– (2)H – (6)OH
ΔE (eV)	0.97	0.99	0.99	0.99
VDE (eV)	**3.32**	**3.93**	**4.31**	**4.19**
Optimized Anionic structure				
Structural Polymorphism	β–D–pyranose – (2)H – (6)OH	open chain (A) – (4)H – (6)OH	β–D–furanose– (1)H – (6)OH	open chain (A) – (4)H – (5)OH
ΔE (eV)	0.99	1.03	1.07	1.08
VDE (eV)	**4.20**	**3.80**	**3.89**	**4.01**

Optimized Anionic structure				
Structural Polymorphism	β–D–furanose–(1)H – (3)OH	β–D–furanose–(3)H – (2)OH	open chain (A) – (6)H – (3)OH	β–D–pyranose – (2)H – (4)OH
ΔE (eV)	1.12	1.16	1.17	1.17
VDE (eV)	**3.86**	**3.71**	**4.01**	**3.32**
Optimized Anionic structure				
Structural Polymorphism	β–D–pyranose – (5)H – (2)OH	β–D–furanose–(1)H – (5)OH	open chain (C) – (6)H – (4)OH	β–D–furanose–(2)H – (5)OH
ΔE (eV)	1.18	1.19	1.25	1.26
VDE (eV)	**4.18**	**3.42**	**5.37**	**4.05**
Optimized Anionic structure				
Structural Polymorphism	β–D–furanose–(1)H – (2)OH	β–D–pyranose – (6)H – (5)OH	β–D–furanose–(3)H – (5)OH	open chain (A) – (6)H – (4)OH
ΔE (eV)	1.26	1.27	1.27	1.29
VDE (eV)	**3.79**	**5.57**	**3.93**	**3.24**
Optimized Anionic structure				
Structural Polymorphism	β–D–pyranose – (1)H – (6)OH	β–D–pyranose – (3)H – (6)OH	open chain (A) – (3)H – (6)OH	open chain (A) – (4)H – (6)OH
ΔE (eV)	1.29	1.37	1.39	1.33
VDE (eV)	**4.38**	**3.90**	**3.96**	**3.31**
Optimized Anionic structure				
Structural Polymorphism	β–D–pyranose – (2)H – (3)OH	open chain (A) – (2)H – (3/4)OH	open chain (A) – (6)H – (3/4)OH	β–D–pyranose – (2)H – (6)OH
ΔE (eV)	1.33	1.34	1.36	1.37
VDE (eV)	**3.51**	**5.06**	**5.23**	**3.76**

Optimized Anionic structure				
Structural Polymorphism	β–D–furanose – (1)H – (3)OH	open chain (A) – (3)H – (5)OH	β–D–furanose– (4C)H – (3)OH	β–D–furanose – (5)H – (3)OH
ΔE (eV)	1.42	1.43	1.47	1.50
VDE (eV)	**3.66**	**3.42**	**0.58**	**3.53**
Optimized Anionic structure				
Structural Polymorphism	β–D–furanose – (2)H – (3)OH	β–D–furanose– (2)H – (3)OH	open chain (A) – (6)H – (5)OH	open chain (A) – (6)H – (5)OH
ΔE (eV)	1.50	1.50	1.51	1.55
VDE (eV)	**3.14**	**3.13**	**3.29**	**3.38**
Optimized Anionic structure				
Structural Polymorphism	β–D–furanose – (3)H – (1)OH	β–D–furanose – (1)H – (2)OH	β–D–pyranose – (2)H – (1)OH	β–D–furanose– (2)H – (1)OH
ΔE (eV)	1.57	1.62	1.75	1.76
VDE (eV)	**2.76**	**3.18**	**3.08**	**2.42**
Optimized Anionic structure				
Structural Polymorphism	open chain (A) – (2)H – (3/4)OH	β–D–pyranose – (3)H – (5)OH	open chain (A) – (4)H – (5)OH	β–D–pyranose – (1)H – (5)OH
ΔE (eV)	1.79	1.82	1.85	1.86
VDE (eV)	**5.90**	**4.62**	**3.11**	**5.76**
Optimized Anionic structure				
Structural Polymorphism	β–D–pyranose – (6)H –	β–D–pyranose – (6)H – (2)OH	open chain (B) – (6)H – (4)OH	β–D–furanose – (5)H – (6)OH

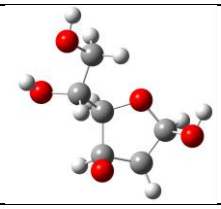
	(3)OH			
ΔE (eV)	1.88	2.02	2.07	2.16
VDE (eV)	**3.72**	**4.20**	**3.13**	**2.58**
Optimized Anionic structure				
Structural Polymorphism	β–D–furanose – (3)H – (2)OH			
ΔE (eV)	2.21			
VDE (eV)	**2.59**			

Figure S9 Optimized geometries of the typical low energy anionic isomers of (mannose – $H_2O)^-$ based on B3LYP/6–311++G(d,p) calculations. The relative energies and structural polymorphs are indicated. The structural presentation is the same as those in the main text Figures 4-9. For open chain structures (1)C to (5)C is ordered from left to right. For both furanose and pyranose structures (1)C to (5)C is ordered from right to left in a clockwise direction.