## 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<sub>2</sub>O)<sup>-</sup>, (arabinose-H<sub>2</sub>O)<sup>-</sup>, (mannose-H<sub>2</sub>O)<sup>-</sup>, and (mannose-H<sub>2</sub>O)<sup>-</sup> 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  $\Leftrightarrow$  Figure 5.

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	2, 3			
Optimized Anionic structure			3.50	
Structural	open chain (B) –	β-furanose – (1)H	open chain (A) –	open chain (A) –
Polymorphism ΔE (eV)	(5C)H 0.00	0.39	(4C)H 0.40	(3)H 0.45
VDE (eV)	3.52	3.82	4.51	4.07
(DE (C1)				
	• • •	• • • • • • • • • • • • • • • • • • •	39 33	
Optimized Anionic structure		3		
Structural	open chain (B) – (2)H	open chain (B) – (2C)H	open chain (A) – (2C)H	β-furanose – (1)H
Polymorphism ΔE (eV)	0.52	0.53	0.56	0.63
VDE (eV)	3.96	2.62	2.50	3.92
VDE (ev)	3.70	2.02	2.30	3,74
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
TIDE ( TI)	2.50	2.55	3.67	3.31
VDE (eV)	3.50	3.55	2.07	3.31
Optimized Anionic structure	3.50	3.55		0101
Optimized Anionic structure Structural	open chain (B) –	open chain (A) –	β-pyranose – (4C)H	β-pyranose – (3)H
Optimized Anionic structure				
Optimized Anionic structure Structural Polymorphism	open chain (B) – (3)H	open chain (A) – (4)H	β-pyranose – (4C)H	β-pyranose – (3)H
Optimized Anionic structure Structural Polymorphism ΔE (eV)	open chain (B) – (3)H 0.96	open chain (A) – (4)H 0.97	β-pyranose – (4C)H 0.98	β-pyranose – (3)H 0.98
Optimized Anionic structure Structural Polymorphism ΔE (eV)	open chain (B) – (3)H 0.96	open chain (A) – (4)H 0.97	β-pyranose – (4C)H  0.98  3.35	β-pyranose – (3)H 0.98
Optimized Anionic structure Structural Polymorphism ΔE (eV) VDE (eV)  Optimized Anionic structure Structural	open chain (B) – (3)H 0.96 4.01  open chain (B) –	open chain (A) – (4)H 0.97	β-pyranose – (4C)H  0.98  3.35  open chain (A) –	β-pyranose – (3)H 0.98
Optimized Anionic structure Structural Polymorphism ΔΕ (eV) VDE (eV)  Optimized Anionic structure	open chain (B) – (3)H 0.96 4.01	open chain (A) – (4)H 0.97 3.47	β-pyranose – (4C)H  0.98  3.35	β-pyranose – (3)H 0.98 3.13

			T	T
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	$\beta$ -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)<sup>-</sup> 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	1 1 (D) (0)	11.7	0.0 (1)**	1 1 (1) (2) 77
Structural	open chain $(B) - (2)H -$	open chain (B) –	$\beta$ -furanose – (1)H –	open chain $(A) - (2)H -$
Polymorphism	(4)OH	(5C)H – (3)OH	(5)OH	(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	open chain (B) – (5C)H	open chain (B) –	β-furanose – (3C)H –	open chain (A) – (2C)H
Polymorphism	-(2)OH	(2C)H - (3)OH	(5)OH	- (3)OH
$\Delta E (eV)$	0.49	0.68	0.76	0.91
VDE (eV)	3.80	1.50	1.56	1.36
VDE (EV)	3.00	1.50	1.50	1.50
Optimized Anionic structure		93933	333	
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
$\Delta E (eV)$	1.20	1.25	1.29	1.36
VDE (eV)	4.09	3.54	4.03	2.32
VDE (ev)	4.07	J.J4	4.03	4.34
Optimized Anionic structure	open chain (A) (2CVI	open chain (A) (5)II	B furance (2)H	open chair (P) (2)H
Structural	open chain $(A) - (2C)H$	open chain $(A) - (5)H$	$\beta$ -furanose – (2)H –	open chain (B) – (3)H –
Polymorphism	- (3)OH	- (2)OH	(5)OH	(2)OH

VDE (eV)	Optimized Anionic structure   Open chain (B) - (4)H - Polymorphism   Open chain (B) - (4)H - (2)OH   Open chain (B) - (4)H - (5)OH   Open chain (B) - (2)OH   Open chai					
Optimized Anionic structure           Sructural Polymorphism         (1)OH         — (2)OH         (4)CH         — (5)OH         — (4)OH         — (4)OH         — (4)OH         — (4)OH         — (2)OH         — (2)OH         — (3)OH         — (5)OH	Optimized Anionic structure           Optimized Anionic structure           Optimized Anionic structure           AE (eV)         1.56         1.57         1.59         1.61         Open chain (A) – (3)H – (2)OH         Open chain (B) – (B)H –	$\Delta E (eV)$	1.39	1.41	1.43	1.47
Optimized Anionic structure   Open chain (B) - (4)H - (2)OH   Open chain (A) - (3)H   Optimized Anionic structure   Optimiz	Optimized Anionic structure   Open chain (B) - (4)H - (2)OH   (-4)OH   (	VDE (eV)	1.47	4.25	1.57	3.77
Anionic structure   Structural   Polymorphism   (2)OH	Anionic structure   Structural   Polymorphism   (2)OH   (2)OH   (2)OH   (3)OH   (3)OH   (2)OH   (2)OH   (3)OH   (2)OH   (2)OH   (3)OH   (2)OH   (2)	` ,				
Polymorphism   C2OH	Polymorphism					
Optimized Anionic structure   Structural Polymorphism   C2)OH   AE (eV)   1.76   1.77   1.82     Optimized Anionic structure   Structural Polymorphism   C4)OH   C4	Optimized Anionic structure   Structural Polymorphism   C1)OH	Structural		_		open chain (A) – (3)H – (2)OH
Optimized Anionic structure   Structural Polymorphism   C2)OH   Optimized Anionic structure   Structural Polymorphism   C2)OH   Optimized Anionic structure   Structural Polymorphism   C4)OH   Optimized Anionic structure   Structural Polymorphism   C4)OH   Optimized Anionic structure   Structural Polymorphism   Optimized Anionic structure   Structural Polymorphism   Optimized Anionic structure   Structural Polymorphism   Optimized Anionic structure	Optimized Anionic structure   Structural Polymorphism   ΔΕ (eV)   1.70   1.73   1.74   1.75     Optimized Anionic structure   Structural Polymorphism   CI)OH   Open chain (A) – (3)H   Open chain (B) – (4)OH   Open chain (B) – (5)OH   Open chain (B) – (4)OH   Open chain (B) – (5)OH   Open chain (B) – (4)OH   Open chain (B) – (4)OH   Open chain (B) – (5)OH   Open chain (B) – (4)OH   Open chain (B) – (5)OH   Open chain (B) – (2)OH   Open chai	ΔE (eV)	1.56	1.57	1.59	1.61
Anionic structure   Structural   Open chain (B) – (4)H – (2)OH	Anionic structure   Structural   Open chain (B) – (4)H – (2)OH		3.94	3.96	3.55	3.57
Polymorphism	Polymorphism   (2)OH   (2)OH   (4C)H - (5)OH   (2)OH     AE (eV)					
AE (eV)	AE (eV)	I .				
VDE (eV)         4.05         3.41         1.09         3.36           Optimized Anionic structure           Structural Polymorphism         β-furanose – (3C)H – (2)OH – (2)OH (4C)H – (5)OH – (4)OH – (4)OH         — (4)OH – (5)OH – (4)OH – (4)OH         — (4)OH – (5)OH – (4)OH – (4)OH         — (4)OH – (5)OH – (6)OH	VDE (eV)         4.05         3.41         1.09         3.36           Optimized Anionic structure         β-furanose – (3C)H – (2)OH — (2)OH — (4C)H – (5)OH — (4)OH — (2C)H – (4)OH — (2C)H – (5)OH — (4)OH — (2C)H – (4)OH — (2C)H – (5)OH —	Polymorphism	` /			` ′
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Optimized Anionic structure         β-furanose – (3C)H – (1)OH – (2)OH – (2)OH – (4C)H – (5)OH – (4)OH – (4O)H – (2)OH – (4C)H – (5)OH – (4O)H – (4O)H – (2C)H – (5)OH – (5)	ΔE (eV)				
Anionic structural   Structural   Polymorphism   (1)OH   - (2)OH   (4C)H - (5)OH   - (4)OH   - (4)OH   (4C)H - (5)OH   - (4)OH   - (4)OH   (4C)H - (5)OH   - (4)OH   - (4)OH   - (4)OH   - (2)OH   - (4)OH   - (4)OH   - (2)OH   - (4)OH   - (2)OH   - (4)OH   - (2)OH   - (2)OH	Anionic structural Polymorphism	VDE (eV)	4.05	3.41	1.09	3.36
Polymorphism	Polymorphism	Anionic structure	9 Suppose (2CVI)	anan shair (D) (5)II	an an abain (D)	anan shair (A) (2C)U
ΔΕ (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 – (2C)H – (4)OH         open chain (B) – (2C)H – (5)OH         open chain (A) – (3)H – (5)OH         (5)OH           ΔΕ (eV)         1.76         1.77         1.77         1.82           VDE (eV)         3.41         2.63         2.89         3.62           Structural Polymorphism         open chain (A) – (4C)H – (2)OH         β-furanose – (1)H – (2)OH         open chain (B) – (2)H – (3)OH           ΔΕ (eV)         1.83         1.85         1.86         1.89	ΔΕ (eV)         1.70         1.73         1.74         1.75           VDE (eV)         1.39         3.95         2.67         2.67           Optimized Anionic structural Polymorphism         open chain (A) – (3)H – (2C)H – (4)OH         open chain (B) – (2C)H – (5)OH         open chain (A) – (3)H – (5)OH         (5)OH           ΔΕ (eV)         1.76         1.77         1.77         1.82           VDE (eV)         3.41         2.63         2.89         3.62           Structural Polymorphism         open chain (A) – (4C)H – (2)OH         β-furanose – (1)H – (2)OH         open chain (B) – (2)H – (2)OH         (3)OH           ΔΕ (eV)         1.83         1.85         1.86         1.89		•			
VDE (eV)         1.39         3.95         2.67         2.67           Optimized Anionic structure         Open chain (A) – (3)H – (2C)H – (4)OH         Open chain (B) – (2C)H – (5)OH         Open chain (A) – (3)H – (5)OH         Open chain (A) – (3)H – (5)OH         (5)OH           ΔΕ (eV)         1.76         1.77         1.77         1.82           VDE (eV)         3.41         2.63         2.89         3.62           Optimized Anionic structure         Open chain (A) – (4C)H – (2)OH         β-furanose – (1)H – (2)OH         Open chain (B) – (2)H – (3)OH         Open chain (B) – (2)H – (3)OH         (3)OH           ΔΕ (eV)         1.83         1.85         1.86         1.89	VDE (eV)         1.39         3.95         2.67         2.67           Optimized Anionic structure         Open chain (A) – (3)H – (2C)H – (4)OH         Open chain (B) – (2C)H – (5)OH         Open chain (A) – (3)H – (5)OH         (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         Open chain (A) – (4C)H – (2)OH         β-furanose – (1)H – (2)OH         Open chain (B) – (2)H – (2)OH         Open chain (B) – (2)H – (2)OH         (3)OH           ΔE (eV)         1.83         1.85         1.86         1.89					
Optimized Anionic structure           Structural Polymorphism         open chain (A) – (3)H – (2C)H – (4)OH         open chain (B) – (2C)H – (5)OH         open chain (A) – (3)H – (5)OH         open chain (A) – (3)H – (5)OH         (5)OH           VDE (eV)         3.41         2.63         2.89         3.62           Optimized Anionic structure           Structural Polymorphism         open chain (A) – (4C)H – (2)OH         β-furanose – (1)H – (2)OH         open chain (B) – (2)H – (2)OH         (3)OH           ΔΕ (eV)         1.83         1.85         1.86         1.89	Optimized Anionic structure           Structural Polymorphism         open chain (A) – (3)H – (2C)H – (4)OH         open chain (B) – (2C)H – (5)OH         open chain (A) – (3)H – (5)OH         open chain (A) – (3)H – (5)OH         (5)OH           VDE (eV)         3.41         2.63         2.89         3.62           Optimized Anionic structure         Structural Polymorphism         open chain (A) – (4C)H – (2)OH         β-furanose – (1)H – (2)OH         open chain (B) – (2)H – (2)OH         open chain (B) – (2)H – (3)OH         (3)OH           ΔΕ (eV)         1.83         1.85         1.86         1.89	` /				
Anionic structure   Structural   Open chain (A) – (3)H –   Open chain (B) –   Open chain (B) –   Open chain (B) –   Open chain (B) –   Open chain (A) – (3)H – (5)OH	Anionic structure   Structural   Open chain (A) – (3)H – Open chain (B) – (2C)H – (4)OH   (2C)H – (5)OH   (5)OH     ΔΕ (eV)   1.76   1.77   1.77   1.82     VDE (eV)   3.41   2.63   2.89   3.62     Optimized   Anionic structure   Structural   Open chain (A) – (4C)H   Polymorphism   – (3)OH   (2)OH   (2)OH   (2)OH   (3)OH     ΔΕ (eV)   1.83   1.85   1.86   1.89	VDE (EV)	1.37	3.73	2.07	2.07
Polymorphism         (4)OH         (2C)H – (4)OH         (2C)H – (5)OH         (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         β-furanose – (1)H – (2)OH         (2)OH         (2)OH         (3)OH         (3)OH<	Polymorphism         (4)OH         (2C)H – (4)OH         (2C)H – (5)OH         (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         β-furanose – (1)H – (2)OH         (2)OH         (2)OH         (3)OH         (3)OH         (2)OH         (3)OH         (3)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 (2)OH (2)OH (2)OH (2)OH (3)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 – (2)OH – (2)OH – (2)OH – (2)OH – (3)OH –					
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       open chain (B) – (2)H – (3)OH       <	VDE (eV)         3.41         2.63         2.89         3.62           Optimized Anionic structure         Structural Polymorphism         open chain (A) – (4C)H – (2)OH         β-furanose – (1)H – (2)OH         open chain (B) – (2)H – (3)OH         (3)OH <td></td> <td></td> <td></td> <td></td> <td></td>					
Optimized Anionic structure         Open chain (A) – (4C)H         β-furanose – (1)H –         β-furanose – (1)H –         open chain (B) – (2)H –           Structural Polymorphism         – (3)OH         (2)OH         (2)OH         (3)OH           ΔE (eV)         1.83         1.85         1.86         1.89	Optimized Anionic structure         Open chain (A) – (4C)H         β-furanose – (1)H –         β-furanose – (1)H –         open chain (B) – (2)H –           Structural Polymorphism         – (3)OH         (2)OH         (2)OH         (3)OH           ΔE (eV)         1.83         1.85         1.86         1.89					
Anionic structureAnionic structureβ-furanose – (1)H – Polymorphismβ-furanose – (1)H – (2)OHβ-furanose – (1)H – (2)OHφ-furanose – (1)H – (2)OHφ-furanose – (1)H – (3)OH $\Delta E$ (eV)1.831.851.861.89	Anionic structureAnionic structureβ-furanose – (1)H – Polymorphismβ-furanose – (1)H – (2)OHβ-furanose – (1)H – (2)OHφ-furanose – (1)H – (2)OHφ-furanose – (1)H – (3)OHΔE (eV)1.831.851.861.89	VDE (CV)	J.71	<b>2.03</b>	<b>2.</b> U)	J.U2
Polymorphism         - (3)OH         (2)OH         (2)OH         (3)OH           ΔΕ (eV)         1.83         1.85         1.86         1.89	Polymorphism         - (3)OH         (2)OH         (2)OH         (3)OH           ΔE (eV)         1.83         1.85         1.86         1.89					
ΔE (eV) 1.83 1.85 1.86 1.89	ΔE (eV) 1.83 1.85 1.86 1.89			•		open chain (B) – (2)H –
		Polymorphism	1 1	` /	` '	` '
VDE (eV) 0.41 3.40 3.39 3.21	VDE (eV)         0.41         3.40         3.39         3.21	ΔE (eV)				
		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
$\Delta E (eV)$	1.92	1.92	1.92	1.93
VDE (eV)	3.97	3.20	0.83	3.28
VDE (CV)	3.71	3.20	0.03	3.20
Optimized Anionic structure				
Structural	open chain $(B) - (4)H -$	open chain $(A) - (2)H$	open chain (A) –	β-pyranose – (1)H –
Polymorphism	(3)OH	- (5)OH	(3)H - (5)OH	(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	open chain $(B) - (4)H -$	open chain $(B) - (2)H$	open chain (A) –	open chain $(A) - (4)H -$
Polymorphism	(3)OH	- (3)OH	(5)H - (3)OH	(3)OH
ΔE (eV)	1.97	1.97	1.99	2.00
VDE (eV)	3.20	3.56	3.97	3.10
	3.0		<b>→</b> •	• • • • • • • • • • • • • • • • • • • •
Optimized Anionic structure				9300
Structural	open chain $(B) - (5)H -$	0.6	open chain (B) –	1 ' (D) (E)II
		$\beta$ -furanose – (1)H –		open chain $(B) - (5)H -$
Polymorphism	(2)OH	β-furanose – (1)H – (5)OH	(3)H – (4)OH	(3)OH
Polymorphism ΔE (eV)		(5)OH 2.03		_
	(2)OH	(5)OH	(3)H - (4)OH	(3)OH
ΔE (eV)	(2)OH 2.03	(5)OH 2.03	(3)H – (4)OH 2.06	(3)OH 2.06
ΔE (eV)	(2)OH 2.03	(5)OH 2.03	(3)H – (4)OH 2.06	(3)OH 2.06
ΔE (eV)  VDE (eV)  Optimized	(2)OH 2.03	(5)OH 2.03	(3)H – (4)OH 2.06	(3)OH 2.06
ΔE (eV)  VDE (eV)  Optimized Anionic structure	(2)OH 2.03 <b>4.49</b>	(5)OH 2.03 <b>3.95</b>	(3)H – (4)OH 2.06 3.48	(3)OH 2.06 3.17
ΔE (eV)  VDE (eV)  Optimized Anionic structure Structural	(2)OH 2.03 <b>4.49</b> open chain (A) – (4)H –	(5)OH 2.03 3.95 β-furanose – (5C)H –	(3)H – (4)OH 2.06 3.48 β-furanose – (1)H –	(3)OH 2.06 3.17 open chain (A) – (4C)H
ΔE (eV)  VDE (eV)  Optimized Anionic structure  Structural Polymorphism	(2)OH 2.03 4.49 open chain (A) – (4)H – (3)OH	(5)OH 2.03 3.95  β-furanose – (5C)H – (2)OH	(3)H – (4)OH 2.06 3.48  β-furanose – (1)H – (2)OH	(3)OH 2.06 3.17 open chain (A) – (4C)H – (3/4)OH
ΔE (eV)  VDE (eV)  Optimized Anionic structure  Structural Polymorphism ΔE (eV)	(2)OH 2.03 4.49 open chain (A) – (4)H – (3)OH 2.10	(5)OH 2.03 3.95  β-furanose – (5C)H – (2)OH 2.11	(3)H – (4)OH  2.06  3.48  β-furanose – (1)H – (2)OH  2.15	(3)OH 2.06 3.17 open chain (A) – (4C)H – (3/4)OH 2.21
ΔE (eV)  VDE (eV)  Optimized Anionic structure  Structural Polymorphism  ΔE (eV)  VDE (eV)  Optimized Anionic structure	(2)OH 2.03 4.49 open chain (A) – (4)H – (3)OH 2.10 3.26	(5)OH 2.03 3.95  β-furanose – (5C)H – (2)OH 2.11 3.24	(3)H – (4)OH  2.06  3.48  β-furanose – (1)H – (2)OH  2.15  3.19	(3)OH 2.06 3.17 open chain (A) – (4C)H – (3/4)OH 2.21 3.89
ΔE (eV)  VDE (eV)  Optimized Anionic structure  Structural Polymorphism  ΔE (eV)  VDE (eV)  Optimized Anionic structure  Structural	(2)OH 2.03 4.49  open chain (A) – (4)H – (3)OH 2.10 3.26  β-pyranose – (3)H –	(5)OH 2.03 3.95  β-furanose – (5C)H – (2)OH 2.11 3.24  open chain (B) – (5)H	(3)H – (4)OH  2.06  3.48  β-furanose – (1)H – (2)OH  2.15  3.19  β-furanose – (3)H –	(3)OH 2.06 3.17 open chain (A) – (4C)H – (3/4)OH 2.21 3.89 open chain (B) – (2C)H
ΔE (eV)  VDE (eV)  Optimized Anionic structure  Structural Polymorphism  ΔE (eV)  VDE (eV)  Optimized Anionic structure	(2)OH 2.03 4.49 open chain (A) – (4)H – (3)OH 2.10 3.26	(5)OH 2.03 3.95  β-furanose – (5C)H – (2)OH 2.11 3.24	(3)H – (4)OH  2.06  3.48  β-furanose – (1)H – (2)OH  2.15  3.19	(3)OH 2.06 3.17 open chain (A) – (4C)H – (3/4)OH 2.21 3.89

VDE (eV)	2.93	3.48	3.73	3.56
Optimized Anionic structure				
Structural	β-pyranose – (4C)H –	β-pyranose – (3)H –	open chain (A) –	β-furanose – (3C)H –
Polymorphism	(2)OH	(2)OH	(2C)H - (2)OH	(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	open chain (B) – (4)H –	β-furanose – (5C)H –	β-furanose– (3)H –	β-furanose – (2)H –
Polymorphism	(5)OH	(5)OH	(2)OH	(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	open chain $(B) - (5)H -$	$\beta$ -pyranose – (3)H –	open chain (B) –	open chain $(A) - (5C)H$
Polymorphism	(4)OH	(4)OH	(3)H - (4)OH	- (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	β-furanose – (3)H –	β-pyranose – (4C)H –	β-furanose – (5)H –	
Polymorphism	(1)OH	(4)OH	(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.

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Optimized Anionic	38333	2 2 3		3
structure	• • • • • • • • • • • • • • • • • • • •	<b>,</b>	308	
Structural	Open chian (A) –	Open chian (B) –		0.5.6 (0)**
Polymorphism	(5C)H 0.00	(3C)H 0.05	β-D-furanose – (4C)H 0.21	β-D-furanose – (3)H 0.25
ΔE (eV) <b>VDE (eV)</b>	4.32	3.84	4.43	4.28
(***)				
	ა <b>\$</b>			
	•	333		
Optimized Anionic structure			3 3	
Structural			Open chian (A) –	Open chian (B) –
Polymorphism	β-D-furanose – (1)H	β-D-pyranose – (2)H	(6C)H	(5)H
ΔE (eV)	0.38	0.56	0.58	0.63
VDE (eV)	4.24	4.25	3.85	4.05
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Optimized Anionic			30 3 3 9	3 3 3 3 3
structure	<b>~</b> 3 <b>8</b>	0.7		
Structural	β-D-furanose – (2)H	β-D-pyranose – (4C)H	Open chian (B) – (5)H	Open chian (A) – (6)H
Polymorphism ΔE (eV)	0.65	0.66	0.69	0.70
VDE (eV)	3.96	3.76	3.94	3.85
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Optimized Anionic		<b>32</b>		33333
structure	• 3 3	9 3 3	<i>9</i> 5%	
Structural				Open chian (A) –
Polymorphism	β-D-pyranose – (1)H	$\beta$ -D-pyranose – (1)H	$\beta$ -D-furanose – (1)H	(5)H
ΔE (eV)	0.70	0.71	0.71	0.72
VDE (eV)	4.05	4.05	4.02	4.17
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Optimized Anionic structure	•	42.2	33	
Structural	Open chian (B) –		Open chian (B) –	Open chian (B) –
Polymorphism	(4C)H	$\beta$ -D-pyranose – (3)H	(2)H	(3)H
ΔE (eV)	0.82	0.83	0.83	0.85
VDE (eV)	3.70	3.90	3.76	3.48

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Structural	β-D-furanose – (3C)H	Open chian (A) – (4)H	Open chian (B) – (4)H	Open chian (A) – (3)H
Polymorphism ΔE (eV)	0.87	0.88	0.90	0.97
VDE (eV)	3.50	3.57	4.02	3.55
VDE (CV)	3.30	3.31	7.02	3.33
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Optimized Anionic	3 4000	3 4000		
structure	<b>30</b> 3		*	
Structural	Onen akion (D) (O)II	Open chian (B) –	0 D fragge (2)11	Open chian (B) –
Polymorphism	Open chian (B) – (2)H	(3)H 1.04	$\beta$ -D-furanose – (3)H	(2C)H 1.16
ΔE (eV)	1.00 <b>3.65</b>	3.67	1.14 3.35	2.71
VDE (eV)	3.03	3.07	3.33	2./1
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Optimized Anionic structure		<b>*</b> • • • • • • • • • • • • • • • • • • •	~~~	
Structural		Open chian (A) –		Open chian (A) –
Polymorphism	Open chian (A) – (2)H	(2)H	β-D-furanose – (6)H	(2C)H
ΔE (eV)	1.26	1.26	1.31	1.35
VDE (eV)	3.15	3.15	2.95	2.30
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Optimized Anionic				
structure		30	<b>3</b>	<b>300</b> 300
Structural		Open chian (A) –	Open chian (B) –	Open chian (A) –
Polymorphism	β-D-pyranose – (4)H	(3C)H	(1C)H	(1C)H
ΔE (eV)	1.61	1.96	2.11	2.13
VDE (eV)	2.73	3.05	2.10	1.99
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Optimized Anionic				250
structure	<b>39</b> 3 3		9 3 3	•
Structural		β-D-pyranose –	β-D-pyranose –	β-D-furanose –
Polymorphism	$\beta$ -D-pyranose – (5C)H	(2C)H	(1C)H	(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)<sup>-</sup> 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.

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Optimized Anionic	-52 -3-0 0	• • • • • • • • • • • • • • • • • • • •		
structure	1 . (4) (6)11		•	
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Structural		open chain (A) –	open chain $(A) - (4)H$	open chain $(B) - (4)H$
Polymorphism	(4)OH	(6)H – (4)OH	- (2)OH	- (2)OH
ΔE (eV)	0.00	0.03	0.03	0.64
VDE (eV)	2.30	1.91	1.50	1.11
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Optimized Anionic			4 3 4 6 4 Y	
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	open chain $(A) - (3)H$			
Structural	-	open chain (A) -	open chain (A) – (6)H	open chain (A) –
Polymorphism	(2)OH	(6)H - (2)OH	- (2)OH	(2C)H - (3)OH
ΔE (eV)	0.68	0.68	0.70	0.71
VDE (eV)	4.09	4.30	4.10	0.87
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	open chain $(C) - (4)H$			
Structural	_	open chain (A) –	open chain $(A) - (3)H$	$\beta$ –D–furanose – (3)H –
Polymorphism	(2)OH	(5)H - (2)OH	- (6)OH	(1)OH
ΔE (eV)	0.75	0.82	0.91	0.97
VDE (eV)	3.90	4.10	4.19	3.32
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structure	• • • • • • • • • • • • • • • • • • •		<b>~</b>	<u> </u>
Structural	β–D–furanose–	β–D–furanose–	β–D–furanose–	β–D–furanose–
Polymorphism	(3)H - (1)OH	(3)H - (6)OH	(4C)H – (6)OH	(2)H - (6)OH
$\Delta E (eV)$	0.97	0.99	0.99	0.99
VDE (eV)	3.32	3.93	4.31	4.19
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structure		- J	e9 6	300
structure Structural	β–D–pyranose – (2)H	open chain (A) –	β–D–furanose–	open chain (A) – (4)H
structure Structural Polymorphism	- (6)OH	(4)H - (6)OH	(1)H – (6)OH	- (5)OH
structure Structural Polymorphism ΔE (eV)	- (6)OH 0.99	(4)H – (6)OH 1.03	(1)H – (6)OH 1.07	- (5)OH 1.08
structure Structural Polymorphism	- (6)OH	(4)H - (6)OH	(1)H – (6)OH	- (5)OH

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Optimized Anionic	. 20			
structure		3		333
Structural	β–D–furanose–	β–D–furanose–	open chain (A) –	β–D–pyranose –
Polymorphism	(1)H - (3)OH	(3)H - (2)OH	(6)H - (3)OH	(2)H - (4)OH
ΔE (eV)	1.12	1.16	1.17	1.17
VDE (eV)	3.86	3.71	4.01	3.32
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Structural	β–D–pyranose – (5)H	β–D–furanose–	open chain (C) – (6)H	β–D–furanose–
Polymorphism	-(2)OH	(1)H - (5)OH	- (4)OH	(2)H - (5)OH
ΔE (eV)	1.18	1.19	1.25	1.26
VDE (eV)	4.18	3.42	5.37	4.05
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Structural	β–D–furanose–	β–D–pyranose –	β–D–furanose–	open chain (A) –
Polymorphism ΔE (eV)	(1)H – (2)OH 1.26	(6)H – (5)OH 1.27	(3)H – (5)OH 1.27	(6)H – (4)OH 1.29
VDE (eV)	3.79	5.57	3.93	3.24
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Structural Polymorphism	(6)OH	$\beta$ –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
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structure	<b>6</b> ,3		***************************************	13 3
Structural	β–D–pyranose –	open chain (A) –	open chain (A) – (6)H	β–D–pyranose –
Polymorphism	(2)H – (3)OH	(2)H - (3/4)OH	- (3/4)OH	(2)H - (6)OH
ΔE (eV)	1.33	1.34	1.36	1.37
VDE (eV)	3.51	5.06	5.23	3.76

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	$\beta$ –D–furanose – (1)H			
Structural		open chain (A) –	β–D–furanose–	$\beta$ –D–furanose – (5)H –
Polymorphism	(3)OH	(3)H - (5)OH	(4C)H - (3)OH	(3)OH
ΔE (eV)	1.42	1.43	1.47	1.50
VDE (eV)	3.66	3.42	0.58	3.53
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Optimized Anionic	<b>3</b>		<b>5 6</b> 5	
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	β–D–furanose – (2)H	0 D C	1	1 ' / 1 / / / / / / / / / / / / / / / /
Structural	-	β–D–furanose–	open chain (A) –	open chain $(A) - (6)H$
Polymorphism	(3)OH	(2)H - (3)OH	(6)H - (5)OH	- (5)OH
ΔE (eV)	1.50	1.50	1.51	1.55
VDE (eV)	3.14	3.13	3.29	3.38
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Optimized Anionic			32.30	
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Structure	β–D–furanose – (3)H			
Structural		β–D–furanose –	β–D–pyranose –	β–D–furanose–
Polymorphism	(1)OH	(1)H - (2)OH	(2)H - (1)OH	(2)H – (1)OH
	1.57	1.62	1.75	1.76
ΔE (eV) <b>VDE (eV)</b>	2.76	3.18	3.08	2.42
VDE (ev)	2.70	3.10	3.00	2.72
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Optimized Anionic	4			3 3
structure				•
	open chain (A) – (2)H			
Structural		β–D–pyranose –	open chain $(A) - (4)H$	$\beta$ –D–pyranose – (1)H –
Polymorphism	(3/4)OH	(3)H - (5)OH	- (5)OH	(5)OH
$\Delta E (eV)$	1.79	1.82	1.85	1.86
VDE (eV)	5.90	4.62	3.11	5.76
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Optimized Anionic		•	9-0	
structure			<b>40</b> 3 <b>6</b>	3 2
Structural	β–D–pyranose – (6)H	β–D–pyranose –	open chain (B) – (6)H	$\beta$ –D–furanose – (5)H –
Polymorphism	P D Pyranose - (0)11	(6)H - (2)OH	- (4)OH	(6)OH
i orymorphism		(0)11 – (2)011	- (4)011	(0)011

	(3)OH			
ΔE (eV)	1.88	2.02	2.07	2.16
VDE (eV)	3.72	4.20	3.13	2.58
	•3			
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Optimized Anionic structure				
	$\beta$ –D–furanose – (3)H			
Structural	_			
Polymorphism	(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.