^{1}H-NMR: A Novel Approach to Determining the Thermodynamic Properties of Acetaldehyde Condensation Reactions with Glycerol, (+)-Catechin, and Glutathione in Model Wine

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Supporting Information

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Supplementary Table 1a. Assignment of 2D ^{1}H-^{1}H COSY NMR signals to *cis*- and *trans*-dioxolane isomers (**1ab**) in pH 3.5 tartrate buffer with d_4-EtOD

	***cis*-dioxolane**		***trans*-dioxolane**	
Proton Assignment	**Chemical Shift (ppm) and splitting**	**^{1}H-^{1}H COSY Correlations**	**Chemical Shift (ppm) and splitting**	**^{1}H-^{1}H COSY Correlations**
CH_3	1.38, d	5.07	1.35, d	5.16
H_1	5.07, q	1.38	5.16, q	1.35
H_2	3.80, dd	3.96, 4.24	3.65, dd	3.95, 4.08
H_3	3.96, dd	3.80, 4.24	3.95, dd	3.65, 4.08
H_4	4.24, m	3.80, 3.96, 3.58, 3.70	4.08, m	3.65, 3.95, 4.18, 4.27
H_5	3.58, dd	3.70, 4.24	4.18, dd	4.27, 4.08
H_6	3.70, dd	3.58, 4.24	4.27, dd	4.18, 4.08

Supplementary Table 1b. Assignment of 2D ^{1}H-^{1}H COSY NMR signals to *cis*- and *trans*-dioxane isomers (**2ab**) in pH 3.5 tartrate buffer with d_4-EtOD

	***cis*-dioxane**		***trans*-dioxane**	
Proton Assignment	**Chemical Shift (ppm) and splitting**	**COSY Correlations**	**Chemical Shift (ppm) and splitting**	**COSY Correlations**
CH_3	1.30, d	4.87	1.29, d	4.75
H_1	4.87, q	1.30	4.75, q	1.29
H_2	3.94, dd	4.03, 3.69	3.47, dd	3.83, 4.13
H_3	4.03, dd	3.95, 3.69	4.12, dd	3.83, 3.47
H_4	3.69, dd	4.03, 3.95	3.83, dd	3.47, 4.13

Supplementary Table 2. Calculated Equilibrium Constants for the Formation of Dioxane Isomers ($\boldsymbol{K_{dioxanes}}$) versus Dioxolane Isomers ($\boldsymbol{K_{dioxolanes}}$) at pH 3-4, 25-40ºC, and 10x Molar Excess of Glycerol to Acetaldehyde

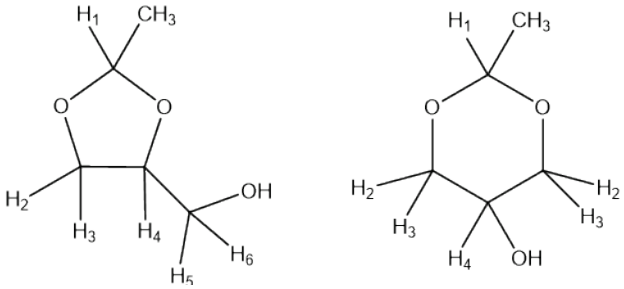
pH	**Temperature**	$\boldsymbol{K_{dioxanes}}$ **(M^{-1})**^{a}	$\boldsymbol{K_{dioxolanes}}$ **(M^{-1})**^{b}	$\frac{\boldsymbol{K_{dioxanes}}}{\boldsymbol{K_{dioxolanes}}}$
3.0	**40**	1.62 ± 0.041	0.908 ± 0.003	1.78
3.5	**25**	0.321 ± 0.010	0.638 ± 0.042	0.504
3.5	**40**	0.807 ± 0.025	0.834 ± 0.062	0.967
3.5	**50**	0.937 ± 0.085	0.775 ± 0.031	1.21
4.0	**40**	0.415 ± 0.00702	0.719± ± 0.0241	0.766

^{a}Calculated using the sum of concentrations for *cis*- and *trans*-dioxane isomers. ^{b}Calculated using the sum of concentrations for *cis*- and *trans*-dioxolane isomers.

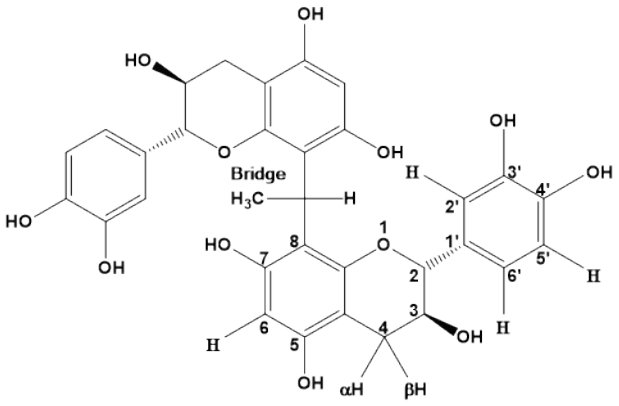
Supplementary Table 3. Assignment of 2D ^{1}H-^{1}H COSY NMR signals to ethylidene-bridged (+)-catechin dimer isomers (**5abc**) in pH 3.5 tartrate buffer with d_4-EtOD

Proton Assignment	^{1}H signals and splitting in monomer	^{1}H signals in dimer (all isomers)[a]	^{1}H-^{1}H couplings
H2	4.74, d	4.49	3.93
		4.59	4.01
		4.63	4.10
H3	4.21, m	3.92	2.41, 2.89, 4.70
		3.93	2.46, 2.78, 4.49
		4.01	2.39, 2.71, 4.59
		4.10	2.43, 2.75, 4.63
H-4α	2.54, dd	2.39	2.71, 4.01
		2.41	2.78, 3.92
		2.43	2.89, 4.10
		2.46	2.75, 3.93
H-4β	2.86, dd	2.71	2.39, 4.01
		2.75	2.46, 4.10
		2.78	2.41, 3.93
		2.89	2.43, 3.92
H6	6.00, s	5.87	
		5.96	
		5.98	
		6.04	
H8	6.09, s	6.13	
		6.17	
		6.23	
H2'	6.92, s	6.66	
		6.74	
		7.03	
		7.06	
H5'	6.91, d	6.72	6.86
		6.77	6.48
		6.82	6.56
		6.83	6.68
H6'	6.84, dd	6.48	6.77
		6.56	6.82
		6.68	6.83
		6.72	6.86

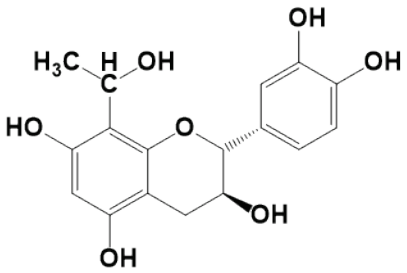
[a]For some signals (H8 and H2), resolution between the two stereoisomers of the 6-8 bridged catechin dimer was not enough to distinguish their signals so only three dimer signals are listed.



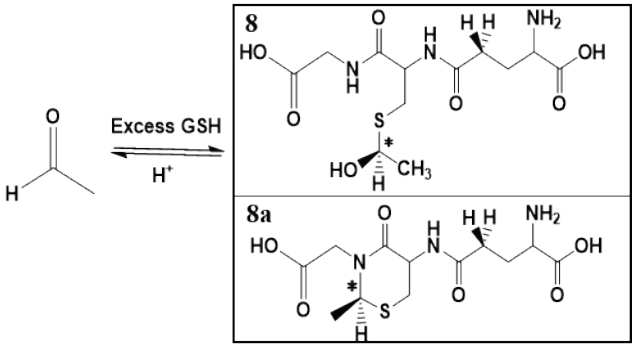
Supplementary Figure 1. Proton assignments for dioxolane (left) and dioxane (right) isomers. Chemical shifts for the protons that were not used for quantitation are reported in Table 1a of the Supplementary Information.



Supplementary Figure 2. Proton assignments for an 8-8 ethylidene-bridged (+)-catechin dimer isomer. 6-6 and 6-8 bridged catechin dimers are also formed.



Supplementary Figure 3. Structure of intermediate in the formation of ethylidene-bridged catechin dimers



Supplementary Figure 4. Two GSH adducts **8** and **8a** are formed when excess GSH is added to acetaldehyde in model wine. For each adduct structure, two stereoisomers are possible as the bonding carbon from acetaldehyde is a chiral center (signified with an asterisk).