Assessing the Potential Mechanisms of Isomerization Reactions of Isoprene Epoxydiols on Secondary Organic Aerosol

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Contents

Synthesis of 2-methyltetrols.

A mixture of 2-methylerythritol and 2-methylthreitol was prepared in two steps. First, (±)-2-methyl-1,2,3,4-diepoxybutane was synthesized based on the procedures of Cole-Filipiak *et. al.*[1] and Wistuba *et al.*[2] 12 mL (110 mmol) of isoprene (Sigma-Aldrich, >99%) was added to a 1 L round-bottom flask containing 600 mL of dichloromethane (Pharmco-Aaper, 99.5%). 56.5g (327 mmol) of *meta*-chloroperoxybenzoic acid (*m*CPBA, Sigma-Aldrich, < 77%) was then added slowly, and the reaction was stirred for 8 days at room temperature. Upon completion of the epoxidation, the majority of the remaining *meta*-chloroperoxybenzoic acid as well as its reduction product, *meta*-chlorobenzoic acid (*m*CBA), were removed by vacuum filtration. Cooling at -20 °C was performed to force more *m*CPBA and *m*CBA out of solution and a second vacuum filtration was performed. The reaction mixture was then washed with a solution of 5% sodium sulfite and saturated sodium carbonate, dried with anhydrous magnesium sulfate, and reduced to approximately 30 mL under reduced pressure. The diepoxide product was isolated using vacuum distillation (30 °C/3 Torr) and characterized using ^{1}H NMR spectroscopy in $CDCl_3$ solvent according to the assignments reported by Wistuba *et al.*

In the second step, the purified diepoxide was combined with 50 mL of deionized water and 100 µL of concentrated H_2SO_4 (Fisher Scientific, 95-98%) in a 500 mL round-bottom flask ([H_2SO_4] = 0.037 M) and stirred for 2 days at room temperature. The reaction mixture was then neutralized to pH 7.0 using 0.1 M NaOH (Sigma-Aldrich, >97%) and concentrated to a slurry under reduced pressure. The 2-methyltetrol products were extracted from the slurry using 80 mL of methanol (Pharmco-Aaper, 99.9%), and the remaining Na_2SO_4 was removed by vacuum filtration. Finally, the methanol solvent was allowed to evaporate, and the resulting 2-methyltetrols were characterized by NMR.

A complete ^{13}C and partial ^{1}H assignment for both diastereomers is given in Figure S1. While the HMQC and HMBC experiments in the present work are sufficient to determine the unique nuclei that belong to a specific diastereomer, the absolute assignment of each set of nuclei to the specific diastereomeric form is based on a match of the present assignment with the partial assignment of the H4 protons to 2-methylerythritol and the H3 protons to 2-methylthreitol reported by Budisulistiorini *et al*.[3]

References

(1) Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J., Kinetics of the hydrolysis of atmospherically relevant isoprene-derived hydroxy epoxides. *Environ. Sci. Technol.* **2010,** *44*, 6718-6723.

(2) Wistuba, D.; Weigand, K.; Peter, H., Stereoselectivity of in vitro isoprene metabolism. *Chem. Res. Toxicol.* **1994,** *7*, 336-343.

(3) Budisulistiorini, S. H.; Li, X.; Bairai, S. T.; Renfro, J.; Liu, Y.; Liu, Y. J.; McKinney, K. A.; Martin, S. T.; McNeill, V. F.; Pye, H. O. T., *et al.*, Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee ground site. *Atmos. Chem. Phys.* **2015,** *15*, 8871-8888.

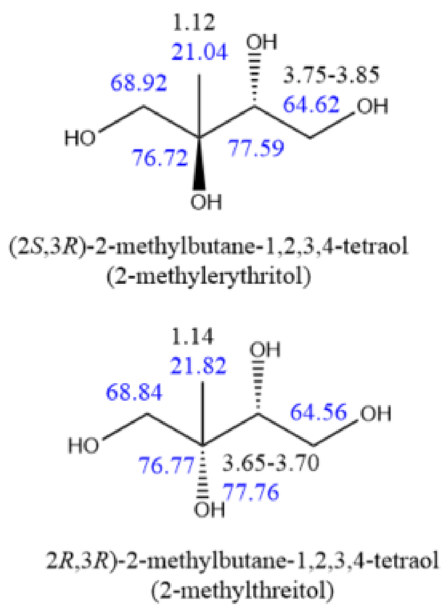
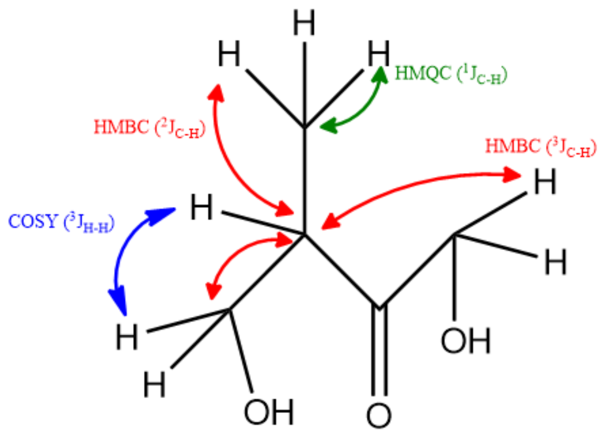


Figure S1: [1]H and [13]C NMR assignments in D_2O for the synthesized 2MTs sample ([1]H NMR assignments in black, referenced to HDO at 4.79 ppm and [13]C NMR assignments in blue, referenced to DSS at 0.0 ppm).



Correlation Technique	Full Name	Correlation Type	Bond Coupling
COSY	^{1}H-^{1}H Correlation Spectroscopy	^{1}H-^{1}H	3
HMQC	^{1}H-^{13}C Heteronuclear Multiple Quantum Correlation Spectroscopy	^{1}H-^{13}C	1
HMBC	^{1}H-^{13}C Heteronuclear Multiple Bond Coherence Spectroscopy	^{1}H-^{13}C	2,3

Figure S2: Correlation NMR spectroscopy methods.

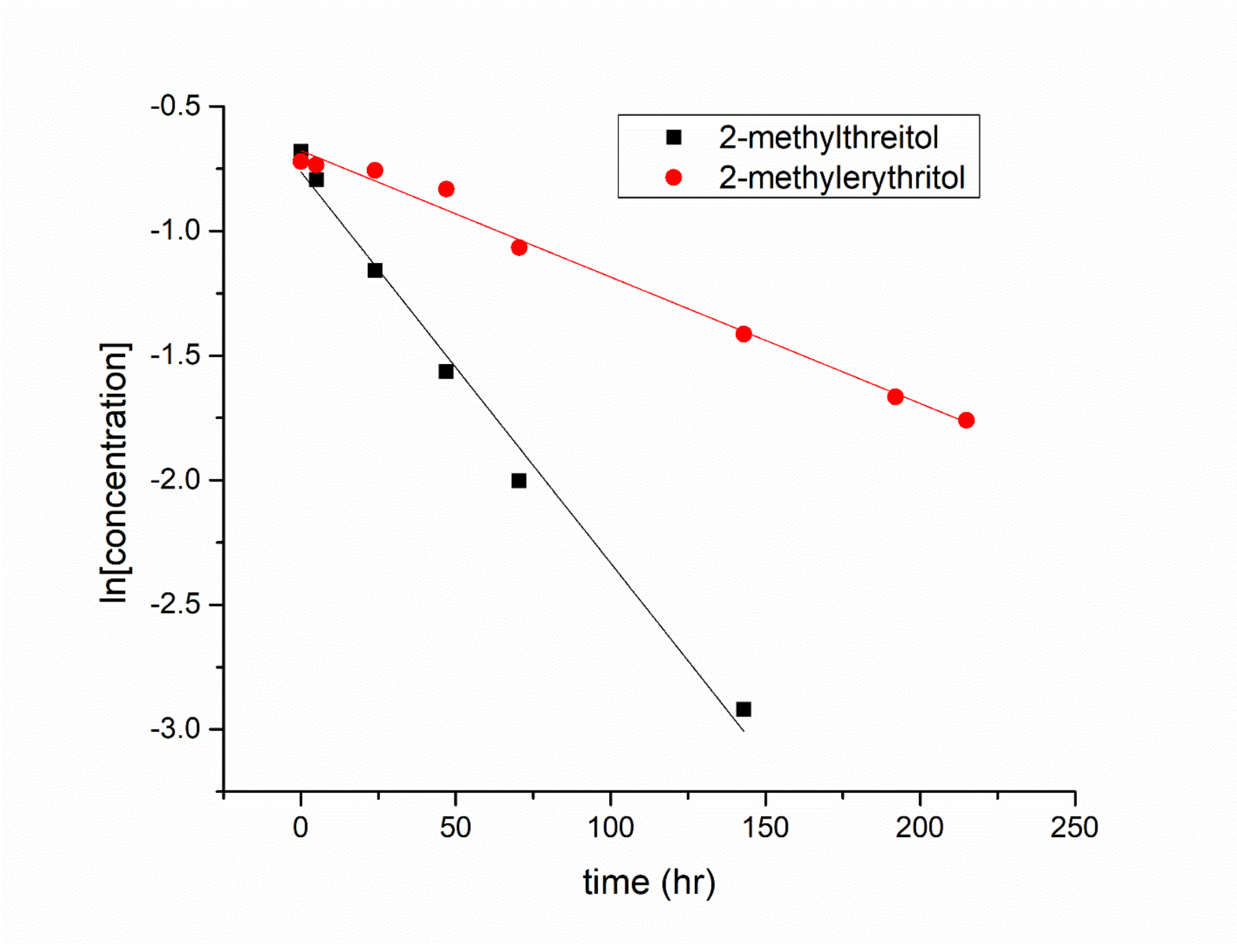


Figure S3: First order kinetics analysis of 2MT diastereomers reacting in 60 wt% $DClO_4$.

reactant	catalyst	τ (d)
1,4-butanediol	70 wt% $DClO_4$	1.29
meso (2R,3S)-butane-1,2,3,4-tetraol (meso-erythritol)	70 wt% $DClO_4$	20.5
(2S,3S)-butane-1,2,3,4-tetraol (D-threitol)	70 wt% $DClO_4$	20.2
racemic (2S,3R and 2R,3S)-2-methylbutane-1,2,3,4-tetraol (2-methylerythritol)	70 wt% $DClO_4$	0.146
racemic (2R,3R and 2S,3S)-2-methylbutane-1,2,3,4-tetraol (2-methylthreitol)	70 wt% $DClO_4$	0.0434
racemic (2S,3R and 2R,3S)-2-methylbutane-1,2,3,4-tetraol (2-methylerythritol)	60 wt% $DClO_4$	8.28
racemic (2R,3R and 2S,3S)-2-methylbutane-1,2,3,4-tetraol (2-methylthreitol)	60 wt% $DClO_4$	2.65

Table S1: First order lifetimes of 1,4-polyols in strong acid aqueous solutions.

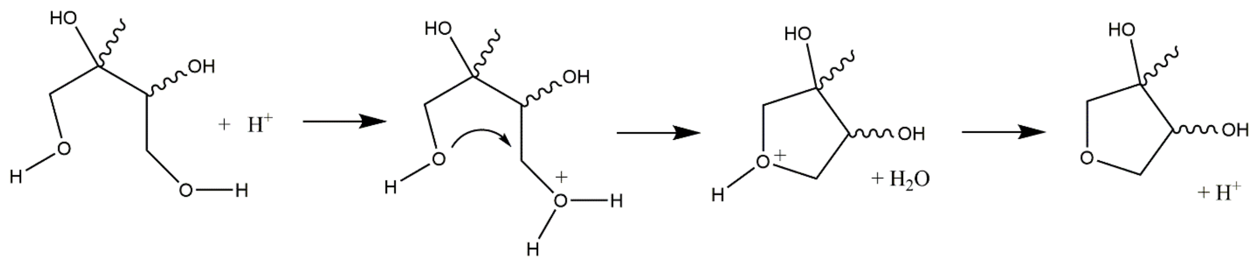
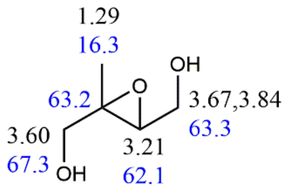
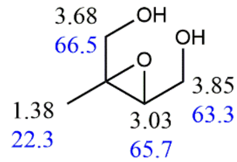


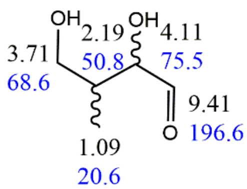
Figure S4: 2MT polyol dehydration cyclization mechanism.



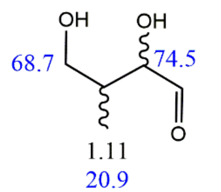
(2-methyloxirane-2,3-diyl)dimethanol
(trans β-IEPOX)



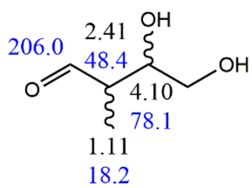
(2-methyloxirane-2,3-diyl)dimethanol
(cis β-IEPOX)



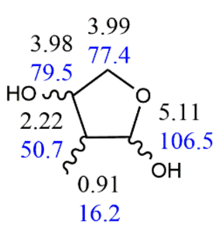
2,4-dihydroxy-3-methylbutanal diastereomer A



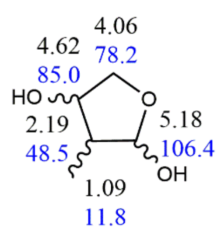
2,4-dihydroxy-3-methylbutanal diastereomer B



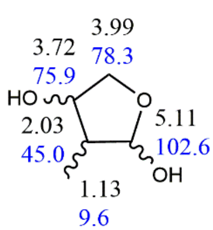
3,4-dihydroxy-2-methylbutanal



3-methyltetrahydrofuran-2,4-diol diastereomer A



3-methyltetrahydrofuran-2,4-diol diastereomer B



3-methyltetrahydrofuran-2,4-diol diastereomer C

Figure S5: ^{1}H and ^{13}C NMR assignments in CD_2Cl_2 for various species identified in the work. ^{1}H NMR assignments in black, referenced to DSS at 0.00 ppm (CD_2Cl_2 at 5.30 ppm) and ^{13}C NMR assignments in blue, referenced to DSS at 0.0 ppm ($CDCl_2$ at 55.7 ppm).

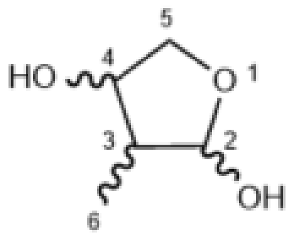
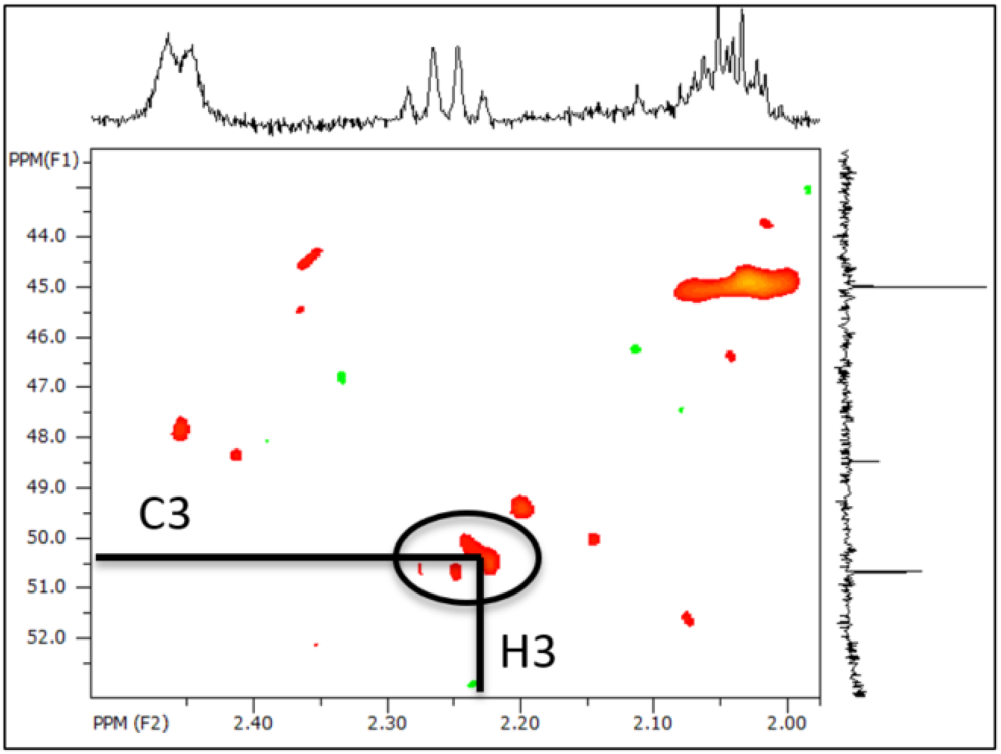
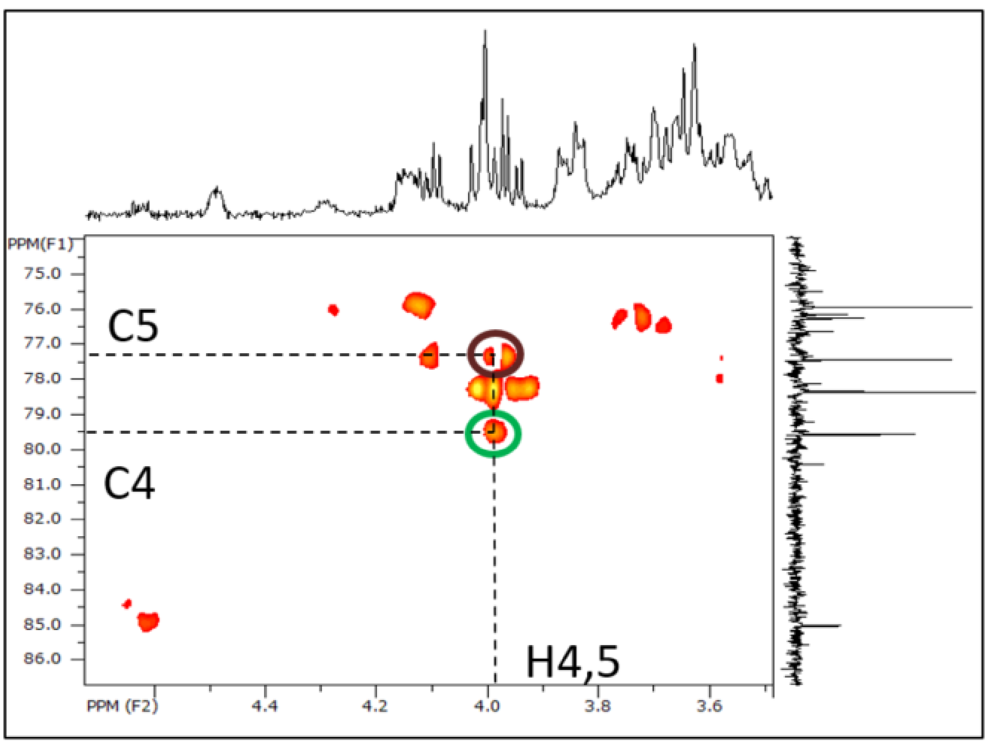


Figure S6: Numbering system for NMR correlation spectroscopy annotations


PPM(F1)
44.0
45.0
46.0
47.0
48.0
49.0
50.0
51.0
52.0
C3
H3
PPM (F2)
2.40
2.30
2.20
2.10
2.00


PPM(F1)
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76.0
77.0
78.0
79.0
80.0
81.0
82.0
83.0
84.0
85.0
86.0
C5
C4
H4,5
PPM (F2)
4.4
4.2
4.0
3.8
3.6

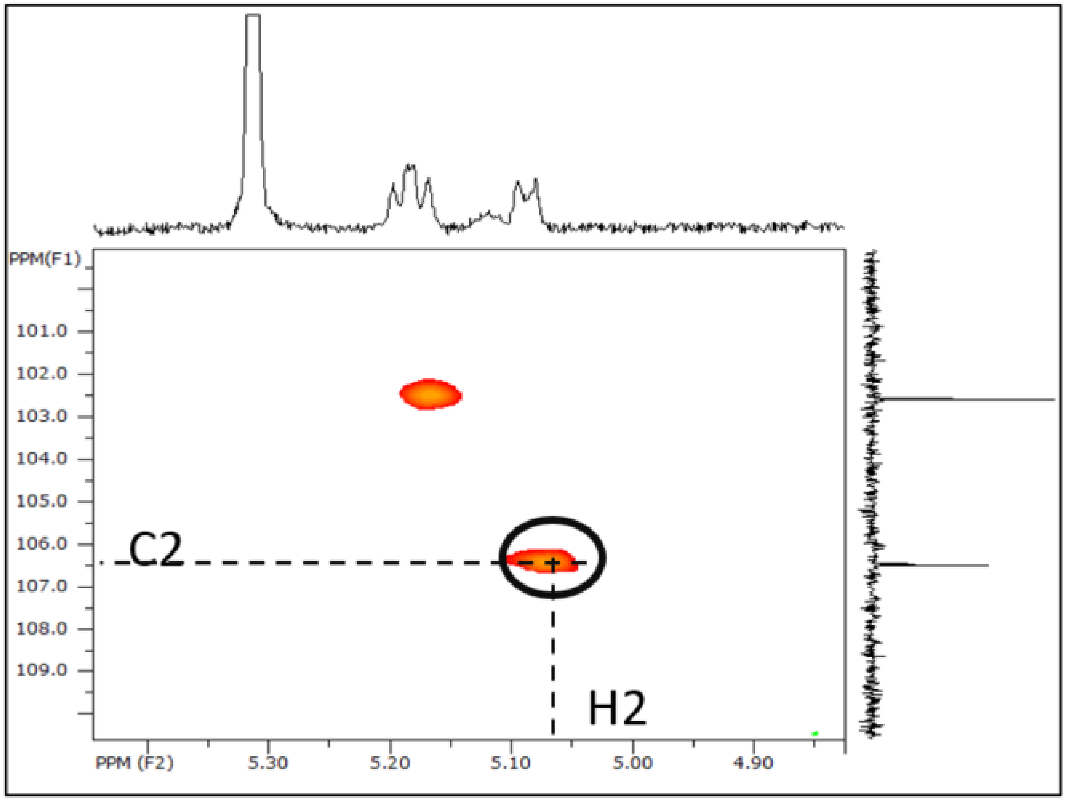


Figure S7: HMQC spectra used for NMR assignments for 3-methyltetrahydrofuran-2,4-diol-A diastereomer

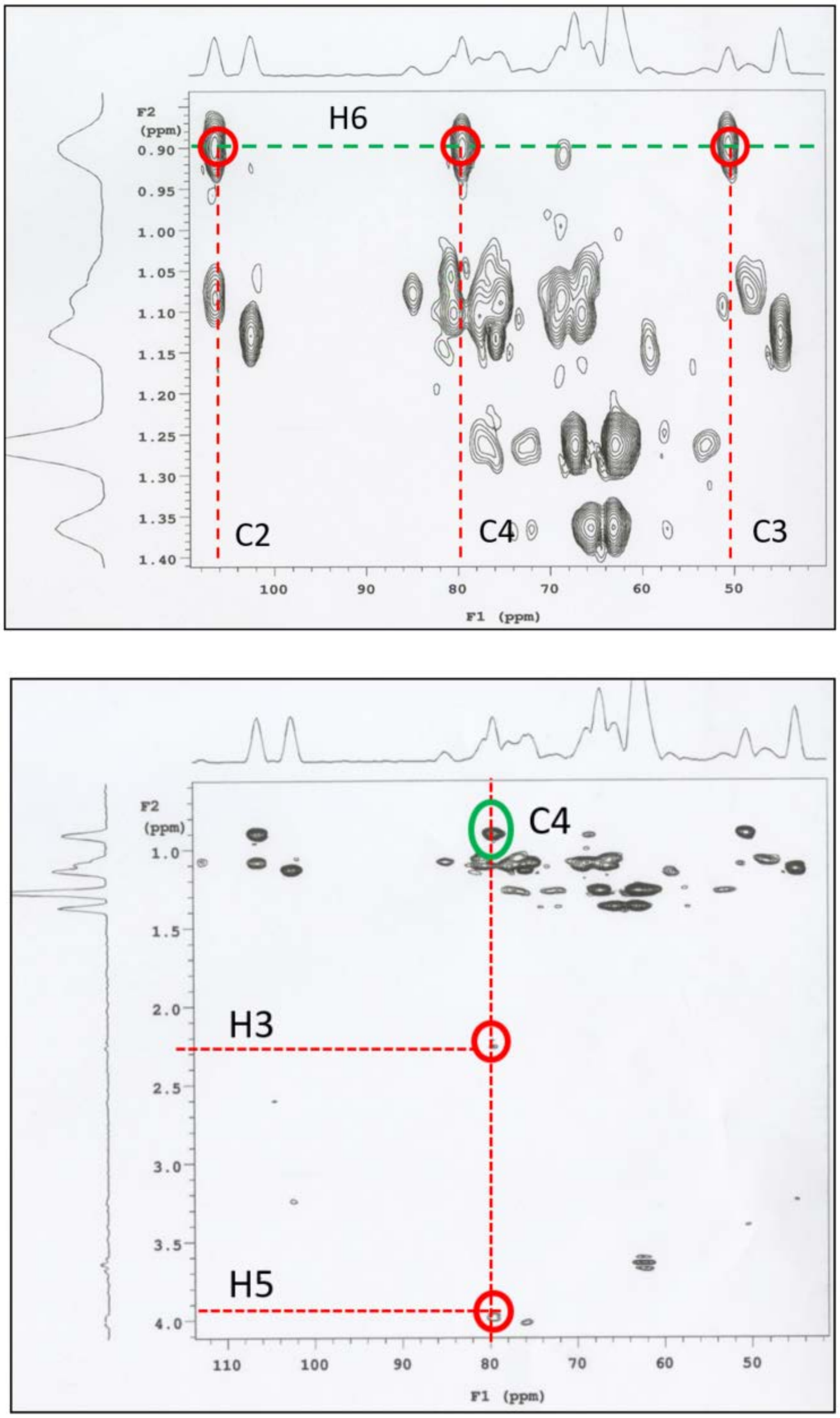


Figure S8: HMBC spectra used for NMR assignments for 3-methyltetrahydrofuran-2,4-diol-A diastereomer

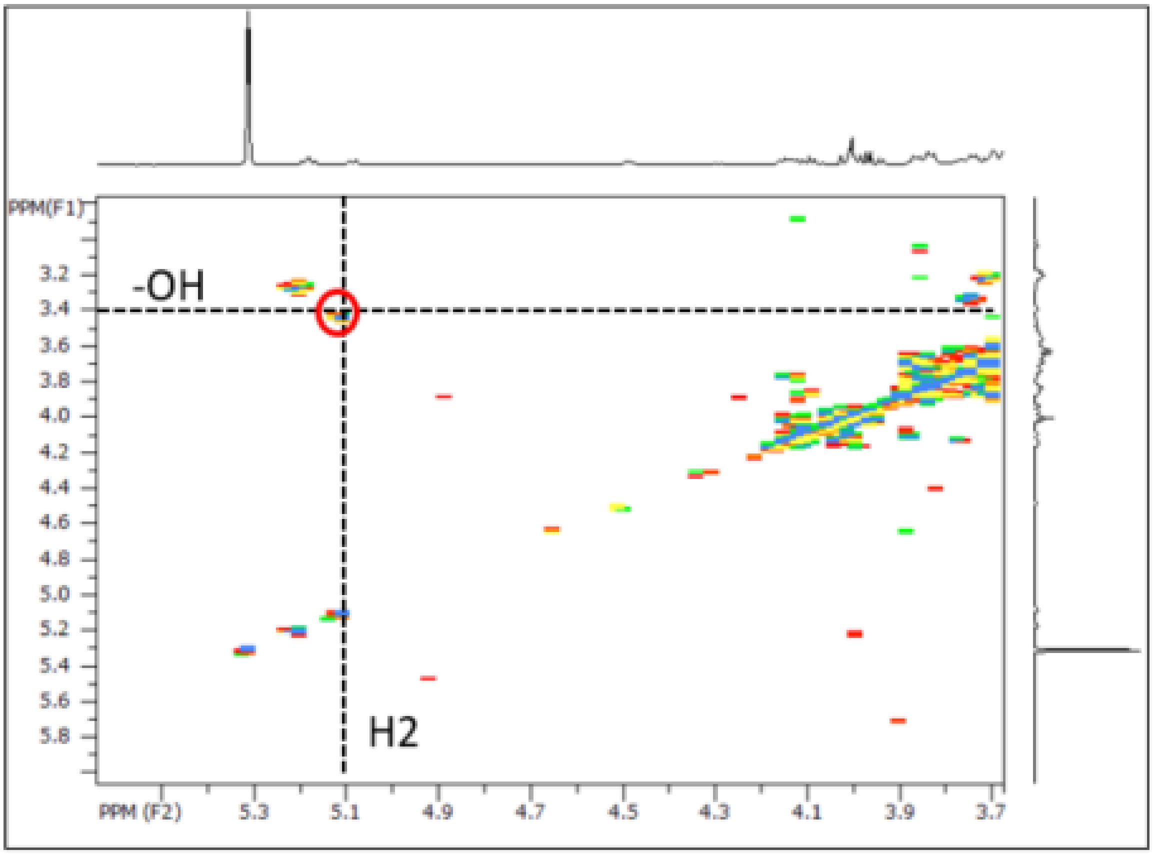
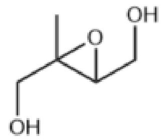
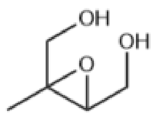
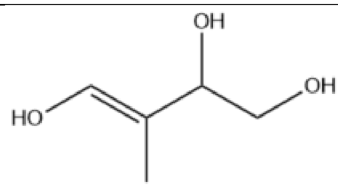
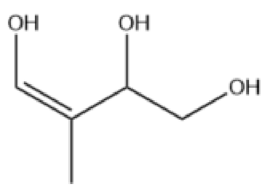
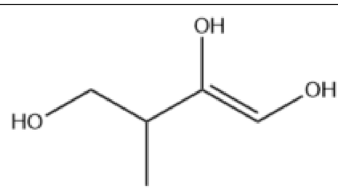
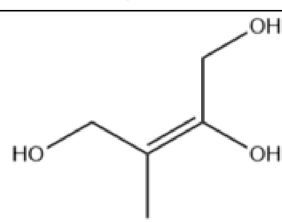
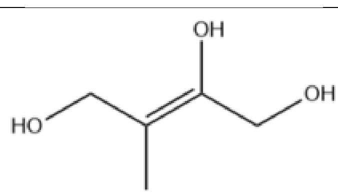
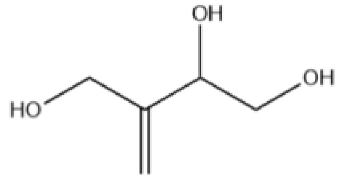
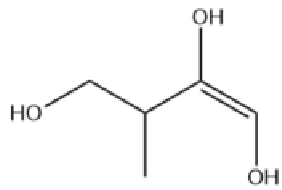
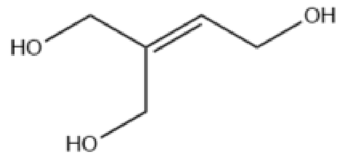
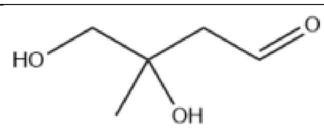
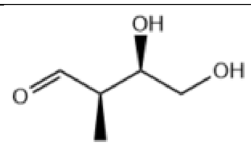
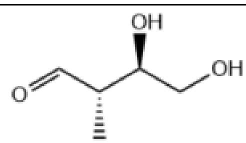
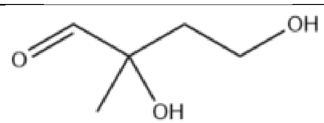
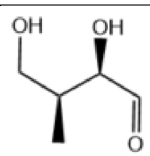
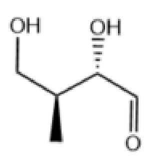
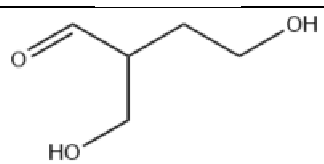
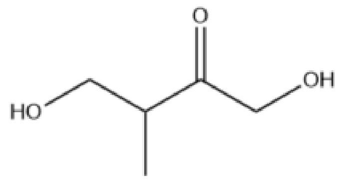
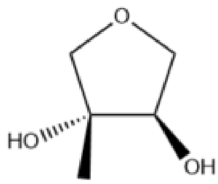
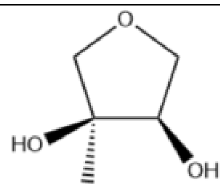
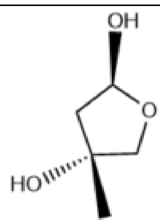
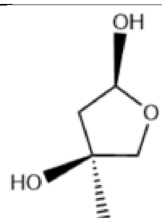
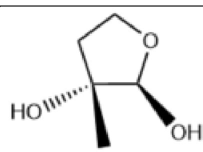
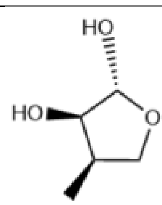
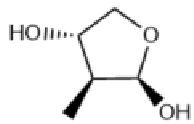
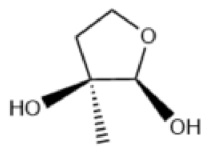
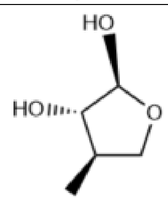
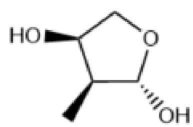
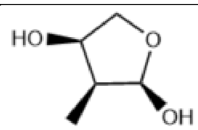
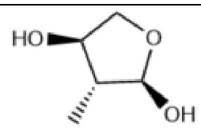
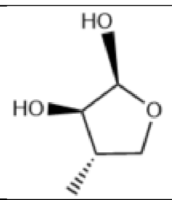
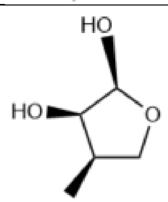
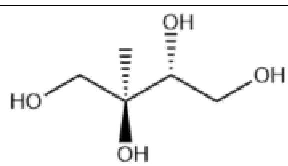


Figure S9: COSY spectrum used for NMR assignments for 3-methyltetrahydrofuran-2,4-diol-A diastereomer

#	Structure	Name	G (kcal/mol)
		epoxides	
1		trans (2-methyloxirane-2,3-diyl)dimethanol (trans β-IEPOX)	+8.4
2		cis (2-methyloxirane-2,3-diyl)dimethanol (cis β-IEPOX)	+11.4
		alkenetriols	
3		(E)-3-methylbut-3-ene-1,2,4-triol	-9.2
4		(Z)-3-methylbut-3-ene-1,2,4-triol	-6.8
5		(Z)-3-methylbut-1-ene-1,2,4-triol	-6.2
6		(E)-3-methylbut-2-ene-1,2,4-triol	-4.0
7		(Z)-3-methylbut-2-ene-1,2,4-triol	-3.9

8		3-methylenebutane-1,2,4-triol	-3.2
9		(E)-3-methylbut-1-ene-1,2,4-triol	-2.9
10		2-(hydroxymethyl)but-2-ene-1,4-diol	+3.1
	aldo diols		
11		3,4-dihydroxy-3-methylbutanal	-15.8
12		(2R,3R)-3,4-dihydroxy-2-methylbutanal	-13.5
13		(2S,3R)-3,4-dihydroxy-2-methylbutanal	-12.6
14		2,4-dihydroxy-2-methylbutanal	-12.2
15		(2R,3S)-2,4-dihydroxy-3-methylbutanal	-11.9
16		(2S,3S)-2,4-dihydroxy-3-methylbutanal	-9.8
17		4-hydroxy-2-(hydroxymethyl)butanal	-8.0

keto diol			
18		1,4-dihydroxy-3-methylbutan-2-one	-14.0
polyol cyclization THFs			
19		(3R,4R)-3-methyltetrahydrofuran-3,4-diol (trans-MeTHF-3,4-diol)	-9.8
20		(3S,4R)-3-methyltetrahydrofuran-3,4-diol (trans-MeTHF-3,4-diol)	-7.6
hemiacetal cyclization THFs			
21		(2S,4R)-4-methyltetrahydrofuran-2,4-diol	-18.5
22		(2S,4S)-4-methyltetrahydrofuran-2,4-diol	-17.1
23		(2R,3R)-3-methyltetrahydrofuran-2,3-diol	-17.0
24		(2R,3R,4R)-4-methyltetrahydrofuran-2,3-diol	-16.2

25		(2R,3S,4S)-3-methyltetrahydrofuran-2,4-diol	-15.9
26		(2R,3S)-3-methyltetrahydrofuran-2,3-diol	-15.7
27		(2S,3S,4R)-4-methyltetrahydrofuran-2,3-diol	-15.6
28		(2S,3S,4R)-3-methyltetrahydrofuran-2,4-diol	-15.4
29		(2R,3S,4R)-3-methyltetrahydrofuran-2,4-diol	-15.0
30		(2R,3R,4R)-3-methyltetrahydrofuran-2,4-diol	-14.9
31		(2S,3R,4S)-4-methyltetrahydrofuran-2,3-diol	-14.2
32		(2S,3R,4R)-4-methyltetrahydrofuran-2,3-diol	-12.3
Hydration species			
33		(2S,3R)-2-methylbutane-1,2,3,4-tetraol (2-methylerythritol)	0.0 (by definition)

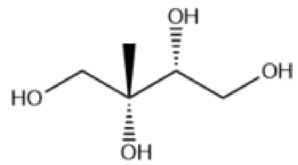
34		(2R,3R)-2-methylbutane-1,2,3,4-tetraol (2-methylthreitol)	+1.5

Table S2: Computed G2MS relative free energies of IEPOX isomers and 2MT isomers in water solvent. A single arbitrary configuration is given above for the cases in which enantiomers are possible because the enantiomeric pairs have identical free energies (i.e., G ((2R,3S,4R)-3-methyltetrahydrofuran-2,4-diol) = G ((2S,3R,4S)-3-methyltetrahydrofuran-2,4-diol)).