Accepted Manuscript

Investigating cyclic sotolon, maple furanone and their dimers in solution using optical rotation, electronic circular dichroism and vibrational circular dichroism

Qin Yang, Miao-Miao Liang, Hui-Jun Wang, Qi-Qi Zhao, Hua-Jie Zhu, Li Liu, Charles U. Pittman, Jr.

PII: S0040-4020(17)30262-4

DOI: 10.1016/j.tet.2017.03.025

Reference: TET 28531

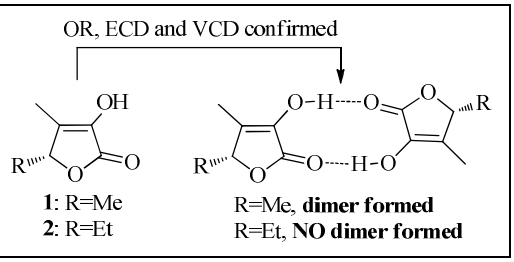
To appear in: *Tetrahedron*

Received Date: 23 December 2016

Revised Date: 4 March 2017

Accepted Date: 10 March 2017

Please cite this article as: Yang Q, Liang M-M, Wang H-J, Zhao Q-Q, Zhu H-J, Liu L, Pittman Jr. CU, Investigating cyclic sotolon, maple furanone and their dimers in solution using optical rotation, electronic circular dichroism and vibrational circular dichroism, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.03.025.

Investigating Cyclic Sotolon, Maple Furanone and their Dimers in Solution Using Optical Rotation, Electronic Circular Dichroism and Vibrational Circular Dichroism	
Qin Yang, Miao-Miao Liang, Hui-Jun Wang, Qi-Qi Zhao, Hua-Jie Zhu, * Li Liu, Charles U. Pittman, Jr.	

Investigating Cyclic Sotolon, Maple Furanone and their Dimers in Solution Using Optical Rotation, Electronic Circular Dichroism and Vibrational Circular Dichroism

Qin Yang, [a] Miao-Miao Liang, [a,1] Hui-Jun Wang, [a] Qi-Qi Zhao, [a] Hua-Jie Zhu, [a]* Li Liu [a], Charles U. Pittman, Jr. [b]

[a]Chinese Center for Chirality, College of Pharmacy, Hebei University, Hebei, China
[b]Department of Chemistry, Mississippi State University, Mississippi State, MS 39763, US

Abstract The experimental optical rotation (OR), electronic circular dichroism (ECD) and vibrational circular dichroism (VCD) spectra of (*R*)-3-hydroxy-4,5-dimethylfuran-2(5H)-one (sotolon, **1**) and (*R*)-5-ethyl-3-hydroxy-4-methylfuran-2(5H)-one (maple furanone, **2**) taken in chloroform were compared to their spectra calculated with time-dependent density functional theory (TDDFT). Sotolon was shown to exist as a dimer in chloroform while maple furanone remains a monomer. Transition state barriers for the enol/keto tautomerization of sotolon were calculated and found to be high. The VCD method offers promise to ultimately distinguish between the presence of monomers or dimers.

Keywords dimer, sotolon, maple furanone, chiroptical spectroscopy

Introduction Optical rotation (OR), electronic circular dichroism (ECD) and vibrational circular dichroism (VCD) methods have been widely used in absolute configuration (AC) assignments.[1-7] VCD is an especially powerful tool for the study of dimeric or polymeric organic chiral compounds in solution. [6] Sotolon (**1**) and maple furanone (**2**) are naturally occurring chiral furanones which are important food additives for wine and maple sugar.[8,9] These 5-substituted-2(5H)-furanones are industrially significant aroma compounds due to their organoleptic properties and extraordinarily low odor thresholds.[10-12] The ACs of **1** and **2** were assigned as (*R*)-(-)-**1** and (*R*)-(+)-**2** by using a VCD-based approach employing time-dependent density functional theory (TDDFT) [13-21] including B3LYP [22,23] and MWP1MPW91[24,25] functionals using 6-31+G(d) [26] and 6-311++G(2d,p) basis sets. [27] The OR sign of (*R*)-**2** is opposite to that of

[1] M.-M Liang and Q. Yang contributed equally