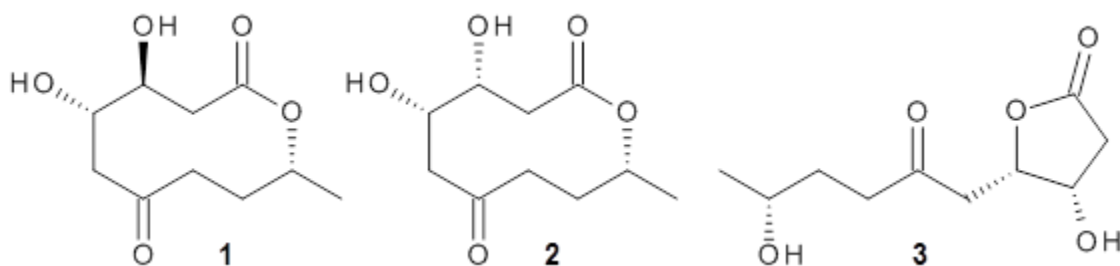


STRUCTURES OF CEPHALOSPOROLIDE C, J, AND BASSIANOLONE

Here is a story that must drive chemical database quality control personnel nuts.

Song, et al. noticed that the reported ^{13}C NMR of the natural products cephalosporolide C **1**, cephalosporolide J **2** and bassianolone **3** are identical.¹ Given that it is highly unlikely that two diastereomers would have identical NMR spectra, the likelihood that these three have identical spectra seemed remote at best.



Compounds **1** and **2** were synthesized and their structures confirmed by x-ray crystallography. Their ^{13}C NMR spectra show clear distinctions, indicating that the isolated “**2**” is actually **1**. Experimental support for the notion that **1** and **3** are actually the same was provided by preparing the diacetylide of **1** and comparing its NMR spectra to that of natural “**3**”.

Quantum computations confirmed that in fact the natural product thought to be **3** is actually **1**. The structures of **1** and **3** were optimized at B3LYP/6-311+G(2d,p) and ^{13}C chemical shifts were computed with these geometries at mPW1PW91/6-311+G(2d,p)/CPCM(chloroform). (The computed structures are shown in Figure 1.) The mean absolute deviation (MAD) between the computed and experimental spectra for **1** is 0.97 ppm, while the MAD for the computed spectrum of **3** compared with the experimental values is 2.44 ppm, with a maximum error of 5.13ppm, more than twice the maximum error with structure **1**. The authors attribute the misassignments to a faulty initial spectra of authentic cephalosporolide C **1**.

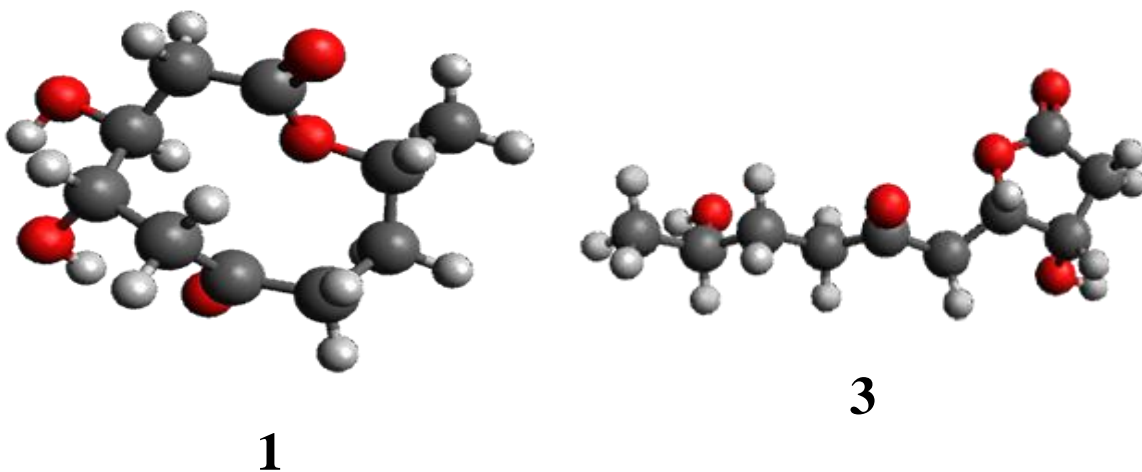


Figure 1. B3LYP/6-311+G(2d,p) optimized geometries of **1** and **3**.

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