^{13}C NMR SPECTROSCOPY OF POLYPHENOL: GIAO/DFT - PW1PW91 CHEMICAL SHIFT CALCULATIONS

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Abstract

Present in almost all plant foods, particularly tea, coffee, wine, fruit, vegetables, wholegrain cereals, and cocoa, Polyphenols are a large and complex family of phytochemicals[1]. Considered a powerful tool for natural product discovery, NMR spectroscopy is used to evaluate a variety of structural features[2]. NMR chemical displacement calculations for natural product structures was pioneered by Bifulco and collaborators and much used to elucidate structures. It occurs that this model had errors of up to 10 ppm for chemical displacement of ^{13}C in NMR. In order to have a good balance between accuracy and computational cost, Forsyth and Sebag improved the chemical displacement application procedures applying empirical scaling factor procedures. This scale factor is obtained through a linear regression of a set of molecules between the experimental and calculated chemical shift, thus correcting systemic errors in computerized[3]. In this work it was longed to create a ^{13}C NMR chemical shift protocol for polyphenols based on the application of scaling factor with twenty chalcones molecules. The protocol consists of values calculated using the GIAO/DFT approach at the level of the predicted ^{13}C chemical shifts (δ_{calc}) for the studied compound and the results are correlated to the experimental NMR data (δ_{exp}). The equation was used as the scaling factor ($\delta_{scal} = 1.06.\delta_{calc} - 2.56$). The MAD errors were only about 1.92 (4.31) while the RMSD errors were about 2.54 (5.15), in ppm, before and after (in parenthesis). The significant reductions in MAD and RMSD that occur after the application of the linear scale procedure shows that, as expected, the applied protocol actually is a powerful tool that manages to reduce errors in NMR chemical shift calculated from polyphenols.

[1] Rothwell, Knaze, e Zamora-Ros, "Polyphenols: Dietary assessment and role in the prevention of cancers".
[2] Wang et al., "Relative Configuration of Natural Products Using NMR Chemical Shifts".
[3] de Albuquerque, Ribeiro, e de Amorim, "Structural determination of complex natural products by quantum mechanical calculations of 13C NMR chemical shifts: development of a parameterized protocol for terpenes".