DIFFERENTIATION OF PENTACYCLIC TRITERPENES REGIOISOMERS BY ^{13}C NMR CHEMICAL SHIFT PREDICTION AT THE mPW1PW91/3-21G//PM7 LEVEL OF THEORY

Rênica Alves de Morais Rocha,[1] Thais Forest Giacomello,[1] Fabio Luiz Paranhos Costa[1*].

Universidade Federal de Goiás, Câmpus Cidade Universitária
BR 364, km 195, nº 3800, CEP 75801-615, Jataí, GO, Brasil.

***flpcosta@ufg.br**

Abstract

Triterpenes are a class of natural products with great importance due to their biological and pharmacological activities.[1] These molecules may have complex structures, which makes their structural characterization through routine analytical techniques a difficult task. Despite the recent advances in spectroscopic techniques, cases of revision of erroneously established natural product structures are still to be found in the literature.[2] In this work we intend to test the robustness of a scaling factor based on GIAO//semi-empirical (mPW1PW91/3-21G//PM7)[3] calculations to determine the^{13}C NMR chemical shifts of 6 pentacyclic triterpenes[4] (2 pairs of regioisomers), i.e., α-amyrin (I) – β-amyrin (II) and α-amyrin acetate (III) – β-amyrin acetate (IV), glutinol (V) and glutinol acetate (VI). The scaled chemical shifts were obtained thru the equation: scaled chemical shifts = 1.14 x calculated chemical shifts - 4.7. The results showed that at the mPW1PW91/3-21G//PM7 level of theory it was able to reproduce the experimental data with small errors. After the application of the scaling factor (which intend to cancel systematic errors), the Mean Absolute Deviation and Root Mean Square errors became significantly smaller (almost 50% for all molecules). This means that even low-levels of theory can be used to cancel systematic errors. Thus, we conclude that the level of theory GIAO-mPW1PW91/3-21G together with the use of the scaling factor represented by the linear equation shows an efficient and low cost tool for the calculation of ^{13}C NMR chemical shifts of pentacyclic triterpenes.

---

1. P. Dzuback. M. Hajduch. D. Vydra. A. Hustova. M. Kvasnica. D. Biedermann. Pharmacological activities of natural triterpenoids and their therapeutic implications. Nat. Prod. Rep., 23, 394-411 (2011).
2. K. C. Nicolaou; S. A. Snyder, Ang. Chem. Int. Ed., 44, 1012 (2005).
3. F. L. P. Costa; T. F. Giacomello; R. A. de M. Rocha; A. M. de J. C. Neto; G. V. da S. Mota, Adv. Sci. Eng. Med. 9, 254, (2017).
4. C. E. Fingolo; T. de S. Santos; M. D. M. Vianna Filho; M. A. C. Kaplan, Molecules, 18, 4248 (2013).