

Use of correlations between calculated carbon chemical shift and ^{13}C NMR data to structural analysis of aristolochic acids and aristolactams

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Introdução

Aristolochia, a genus of the Aristolochiaceae family, consists of about 400 species mostly distributed along tropical and subtropical regions of Asia, Africa, and South America. The most characteristic compounds in this genus are aristolactams and aristolochic acids¹, which are structurally represented by aristolactam All (1) and aristolochic acid I (2) in Figure 1. The literature describes a large amount of different structures of aristolactam and aristolochic acid derivatives because all positions on the phenanthrene skeleton may be substituted by hydroxyl, glycosyl, and alkoxyl groups.

An increasing amount of studies correlating calculated and experimental NMR data has substantially contributed to structural elucidation and investigation of the chemical properties of several organic compounds. The present work describes the use of correlations between calculated and experimental carbon chemical shifts of 1 and 2 as model to structural elucidation of aristolactams and aristolochic acids isolated from *Aristolochia* species.

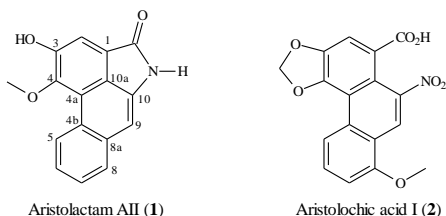


Figure 1. Chemical structure of aristolactam (1) and aristolochic acid (2).

Resultados e Discussão

Different theory levels were employed and the solvent effects were also considered to geometry optimizations and carbon chemical shift calculations of 1 and 2. These compounds were isolated by us from the ethanolic extract of the stem of *Aristolochia esperanzae* and their structures were identified by 1D and 2D NMR².

Theoretical studies were carried out using software package Gaussian 03. The geometries previously obtained from PM3 semi-empirical calculations were used as initial models in geometry optimizations employing HF, DFT, and MP2 calculations with the Pople's split valence base sets 6-31G*, 6-31G**, 6-311G*, 6-311G**, 6-311+G**, and 6-311++G**.

34^a Reunião Anual da Sociedade Brasileira de Química

and 6-311++G**. BLYP, B3LYP, and PBE functionals were used in DFT calculations. The optimized geometries were used to carbon chemical shift calculations at the same levels of theory. Calculated carbon chemical shift values (σ_c) were determined in relation to corresponding calculated values for tetramethylsilane. Correlations between σ_c values and experimental carbon chemical shifts (δ_c) were obtained using software package Origin™ Standard 7.5. The σ_c and δ_c values were plotted on the x and y axes, respectively. The σ_c/δ_c correlation curves were given as linear fits with correlation coefficients (R^2) and slope of the R^2 curve (α) furnished by the program.

Conclusões

The theoretical investigation for structures in the gaseous phase and without considering intermolecular interactions shows that B3LYP/6-31G* ($R^2 = 0.99376$) and PBE/6-311G* ($R^2 = 0.95393$) calculations are the most appropriated theory levels to carbon chemical shift calculations of 1 and 2, respectively. The solvent effect (DMSO) is important factor on carbon chemical shift calculations. The explicit solvent model ($R^2 = 0.99631$ and 0.97774 , by BLYP/6-31G* calculations) was more efficient to carbon chemical shift calculations. The σ_c/δ_c correlation coefficients based on the explicit solvent effect allow appoint the more effective sites of intermolecular interactions between studied compound and the solvent. Dimeric systems 1-1 and 2-2 were also considered using BLYP/6-31G* calculations. The σ_c/δ_c correlation coefficients ($R^2 = 0.99616$ and 0.95065 , respectively) shows that these interactions for the studied compounds are not important to carbon chemical shift calculations.

Agradecimentos

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