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Solamargine and Solamarine: Why so different?

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Introduction:

The Solanaceae family is composed of approximately 2500 species, which include some of the most important species for agriculture. However, the co-occurrence of compounds that exert a negative impact on nutritional quality is a very common problem. Most of the compounds of this type are formed by steroidal alkaloids and steroidal glycoalkaloids, which contribute to plant resistance against pathogens and predators.[1,2] Two of these steroidal glycoalkaloids are Solamargine and Solamarine which differs only in the position of methylene (or amine) group in the heterocyclic ring (figure 1).

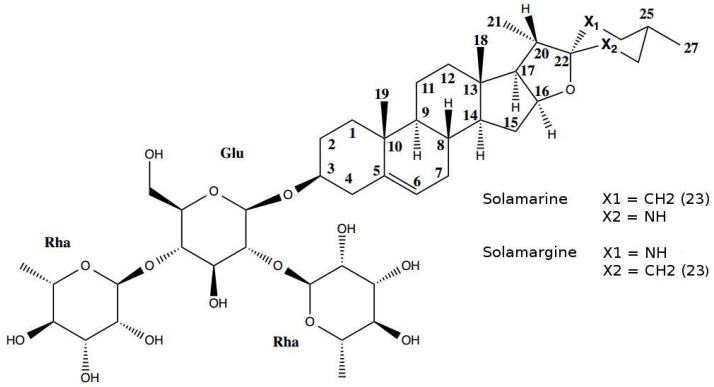

Figure 1: Structures of Solamargine and Solamarine.

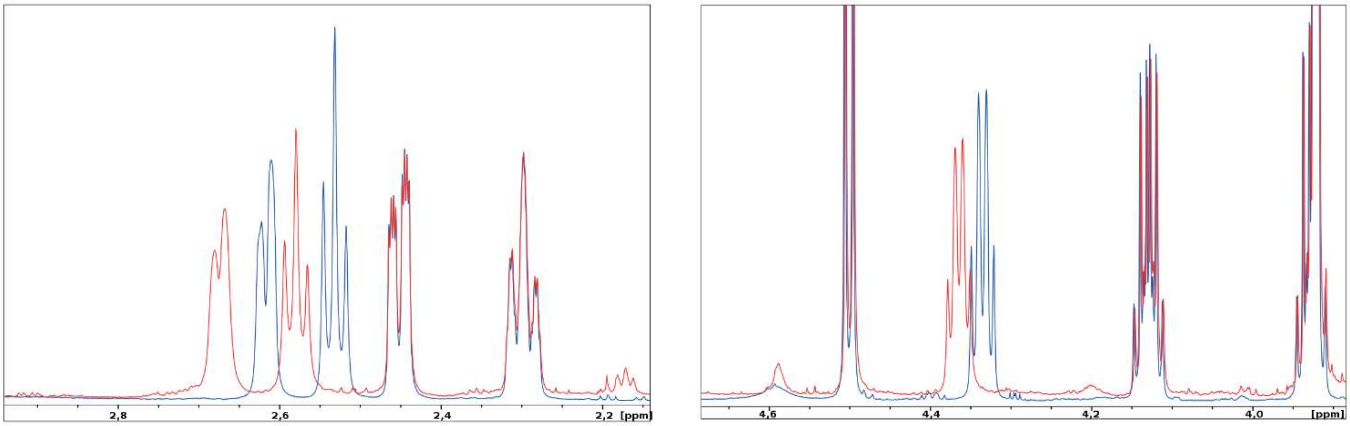

Figure 2: NMR zoomed spectra of Solamargine(blue) and Solamarine (red). On the left the region of H26 (axial and equatorial) chemical shift and on right H16. [800MHz - CD_3OD]

The Solamargine and Solamarine NMR spectra shows a quick difference between chemical shifts of protons of the heterocyclic rings, H16 and H26a and H26e (figure 2).

In order to identify the reason for these differences, NMR (chemical shifts and coupling constant) and NBO calculations were perform.

Results and Discussion:

Conformational analysis of three compounds has led to six conformers for Solamargine, where only three of them have more than 24% of the total population. On the other hand, five conformers were find for Solamarine, only three of them with more than 29% of the total population. Calculations were carry out with Gaussian 09 package at the wB97XD/def2-TZVP level of theory.[3] The Boltzmann averaged calculated chemical shifts and coupling constant are in accordance with the experimental data.

We observe that the differences in spectra are mainly in the chemical shifts of the hydrogen atoms with a heteroatom neighbor (oxygen for H16 and N for H26a and H26e). Based on the observation that the nonbonding electron pairs of the O and N atoms could be, through hyperconjugative effects, the cause of these differences, an NBO analysis was performed.[4] The hyperconjugative effect tends to change the molecular geometric (bond lengths) and electronic parameters of the involved atoms and these changes may led to a change in the NMR data. The effects of hypeconjugation can be infer from the NBO data shown in the table below.

Table 1: NBO data for Solamargine and Solamarine.

	Solamargine		Solamarine	
Atoms	Interaction	Energy (kcal/mol)	Interaction	Energy (kcal/mol)
16	O(LP) → C-H	13,32	O(LP) → C-H	13,44
26a	N(LP) → C-H	11,70	N(LP) → C-H	11,08
26e	N(LP) → C-H	1,45	N(LP) → C-H	1,82

We notice that the hyperconjugative interactions for C-H16 bonds are very similar on both isomers, with a difference of only 0,12 kcal/mol; an effect not so prominent but sufficient to account for the small difference observed in the chemical shifts (spectrum region at the right side of figure 2). On the other hand, for the C-H26, the hyperconjugative transference of electron density is more pronounced (0,62 and 0,39 kcal/mol) and therefore compatible with the greater difference in chemical shifts shown in the spectral region on the left side of figure 2.

Key words: Steroidal alkaloids; NMR; NBO.
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References:

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