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Probing the effect of sugar substitution on the antioxidant-related properties of flavonols

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Abstract: In the recent past, our group did accomplish a computational investigation on two flavonols that were isolated from Loranthaceae family plant extracts: *kaempferol 3-O-α-L-arabinofuranosyl-(1→3)-α-L-rhamnoside* and *quercetin 3-O-α-L-arabinofuranosyl-(1→3)-α-L-rhamnoside* [1], which are glycosylated versions of kaempferol and quercetin, respectively. Among the goals of the referred study was to probe how much the presence of the sugar group would affect the values of bond dissociation enthalpies (BDEs) and ionization potential (IPs) when in comparison with the parent molecules. The BDEs and IPs are important energetic properties in order to investigate the antioxidant potential of a given compound, since they are connected to the hydrogen-atom transfer (HAT) and to the single electron transfer (SET) mechanisms, respectively [2,3]. In the present work, the ideas initiated in de Souza *et al.* [1] were taken further and an investigation on the antioxidant-related properties of *myricetin 3,4'-di-O-alpha-L-rhamnopyranoside* (which is a *myricetin* doubly substituted with the *rhamnopyranoside* moiety) was performed. The structures of the *myricetin 3,4'-di-O-alpha-L-rhamnopyranoside* and its parent molecule is shown in Figure 1.

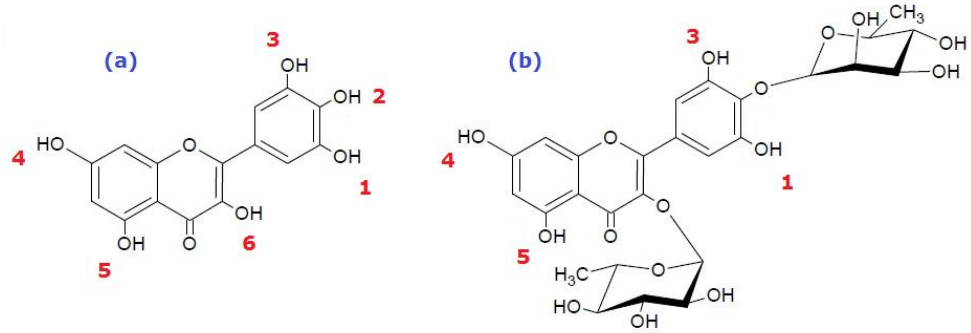

Figure 1. Representation of the chemical structures: (a) *myricetin* and (b) *myricetin 3,4'-di-O-alpha-L-rhamnopyranoside*. OH group numbering is given in red.

The geometries of the neutral molecules and their radicals were optimized (using default convergence criteria) using density functional theory (DFT) with the B3LYP exchange-correlation functional [4,5]. All optimizations were carried out without the inclusion of symmetry constraints. Computations for open-shell species were undertaken with the unrestricted formalism UB3LYP. The 6-311+G(d,p) basis set [6] was utilized. Vibrational frequencies were computed to characterize the conformations as minima, to evaluate the zero-point energy corrections, and to determine

thermodynamic quantities (at 298 K). Solvent effects were included using the integral equation formalism polarizable continuum model for *n*-hexane, methanol, ethanol, and water. All computations were performed with the Gaussian 09 software suite [7].

The BDEs and IPs determined in the gas phase and water are presented in Table 1.

	myricetin				***myricetin 3,4'-di-O-alpha-L-rhamnopyranoside***			
OH group	**BDE**		**IP**		**BDE**		**IP**	
	gas phase	**water**	**gas phase**	**water**	**gas phase**	**water**	**gas phase**	**water**
1	74.99	72.93	162.04	146.58	83.41	81.31	161.11	135.99
2	66.52	64.29			---	---		
3	74.92	72.83			79.50	80.84		
4	86.60	87.18			87.06	86.84		
5	90.49	95.06			97.38	91.95		
6	78.12	82.21			---	---		

Table 2. BDE and IP (given in kcal.mol^{-1}) for *myricetin* and *myricetin 3,4'-di-O-alpha-L-rhamnopyranoside* computed at the B3LYP/6-311+G(d,p) level of theory.

The computed BDEs for *myricetin* have OH group **2** as the smallest followed by groups **3**, **1**, **6**, **4**, and **5**, respectively, indicating that the hydroxyl **2** would be primarily responsible for its antioxidant activity. In the *myricetin 3,4'-di-O-alpha-L-rhamnopyranoside* compound, there are no hydroxyl groups **2** and **6** available due to the substitution; for this compound, BDEs order are **3** < **1** < **4** < **5**. This behavior can be observed for results determined in both gas phase and water. The presence of the substituent leads to an increase in all the BDEs values (except to the groups **4** and **5** computed in water). Hence, the antioxidant activity would be decreased with the inclusion of the *rhamnopyranoside* moiety.

The IPs values present a decrease (more pronounced in water) when the *myricetin* is substituted. However, the IPs are approximately double the BDEs and, thus, the antioxidant activity through the SET mechanism is unlikely to happen. The complete set of results will be presented in the Conference.

Key-words: Antioxidant activity, substituent effect, bond dissociation energy, ionization potential, density functional theory

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