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Peculiarities of 7-hydroxyflavone oxidation in relation to our model for the estimation of the first oxidation potential of flavonoids

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Dear Editor,

in 2023 in your journal I published models for the estimation of the first oxidation potential, E_{p1}, of flavonoids connected with the three different mechanisms of electrochemical oxidation – SET-PT, SPLET, and HAT (1). The models were made on a calibration set of 35 flavonoids for which the oxidation potentials were all measured in our laboratory under the same conditions. The best model was based on the mean values of parameters $\sum_{s(C)} \Delta NAC_{Cat\text{-}Neut}$, $\sum_{s(C)} \Delta NAC_{Rad\text{-}Anion}$ and $\sum_{s(C)} \Delta NAC_{Rad\text{-}Neut}$ as the variable connected with the three different mechanisms of electrochemical oxidation, which should mean that each mechanism contributes to the electrochemical oxidation of every flavonoid pretty much equally.

Recently, I made the same calculations on 7-hydroxyflavone (7-HF, Scheme 1) and obtained 0.623 for $\sum_{s(C)} \Delta NAC_{Cat\text{-}Neut}$, 0.435 for $\sum_{s(C)} \Delta NAC_{Rad\text{-}Anion}$ and 0.321 for $\sum_{s(C)} \Delta NAC_{Rad\text{-}Neut}$. For 7-HF, we did not measure E_{p1}, but since it has only one hydroxyl group placed at the A ring and according to literature (2, 3) its E_{p1} value is similar to that of chrysin and 5-hydroxyflavone. Therefore, I took the mean value of their E_{p1} at pH=3 (1.162 and 1.164, respectively). Placing the data for 7-HF into regressions and figures of dependences of experimental E_{p1} (pH=3) on the differences in the net atomic charges for 35 flavonoids (Models and Figures 2, 3, and 4 in Ref. 1) it is obvious that 7-HF was the only flavonoid that did not fit into any of the three regressions (Figure 1). That would mean that its oxidation mechanism does not correspond to any of the three proposed mechanism of oxidation. However, the mean value of three parameters for 7-HF perfectly fit the best model we obtained for the estimation of the oxidation potential of flavonoids based on the mean values of parameters $\sum_{s(C)} \Delta NAC_{Cat\text{-}Neut}$, $\sum_{s(C)} \Delta NAC_{Rad\text{-}Anion}$ and $\sum_{s(C)} \Delta NAC_{Rad\text{-}Neut}$ (Model and Figure 5 in Ref. 1). Since the model implies that all three mechanisms (SET-PT, SPLET, and HAT) equally contribute to the electrochemical oxidation of all flavonoids, the case of 7-hydroxyflavone would be yet another supporting such a conclusion.

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It is also worth mentioning that the hydroxyl group at position 7 (in the A ring of a flavonoid) is generally the most acidic hydroxyl group in flavonoids, i.e. it deprotonates more easily than the OH group at any other position in a flavonoid (4). It also has the largest value of O-H bond dissociation enthalpy (BDE) and ionisation potential (IP). Thus, it was assumed that the 7-HF mechanism of oxidation corresponds to the sequential proton loss electron transfer (SPLET).

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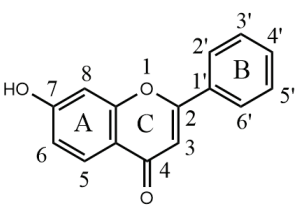

Scheme 1 The structure of 7-hydroxyflavone

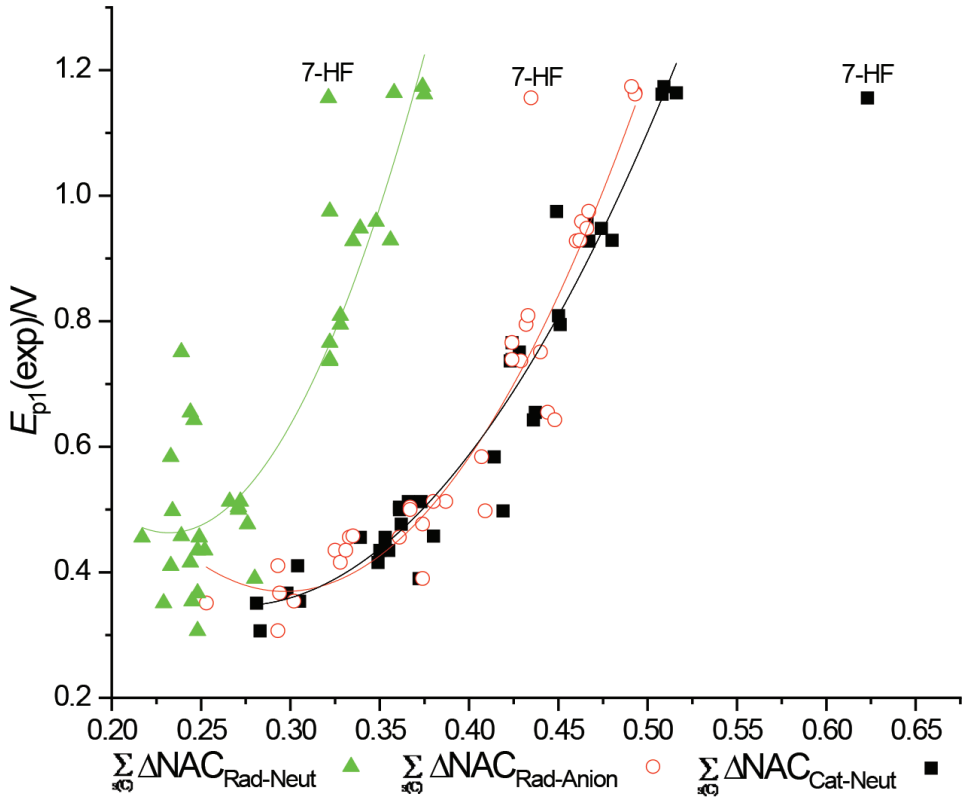

Figure 2 The dependence of experimental E_{p1} (pH=3) on the parameters $\sum_{s(C)} \Delta NAC_{Cat\text{-}Neut}$, $\sum_{s(C)} \Delta NAC_{Rad\text{-}Anion}$ and $\sum_{s(C)} \Delta NAC_{Rad\text{-}Neut}$ (variables 1, 2, and 3) for the set of 35 flavonoids published previously (1), with the addition of 7-HF

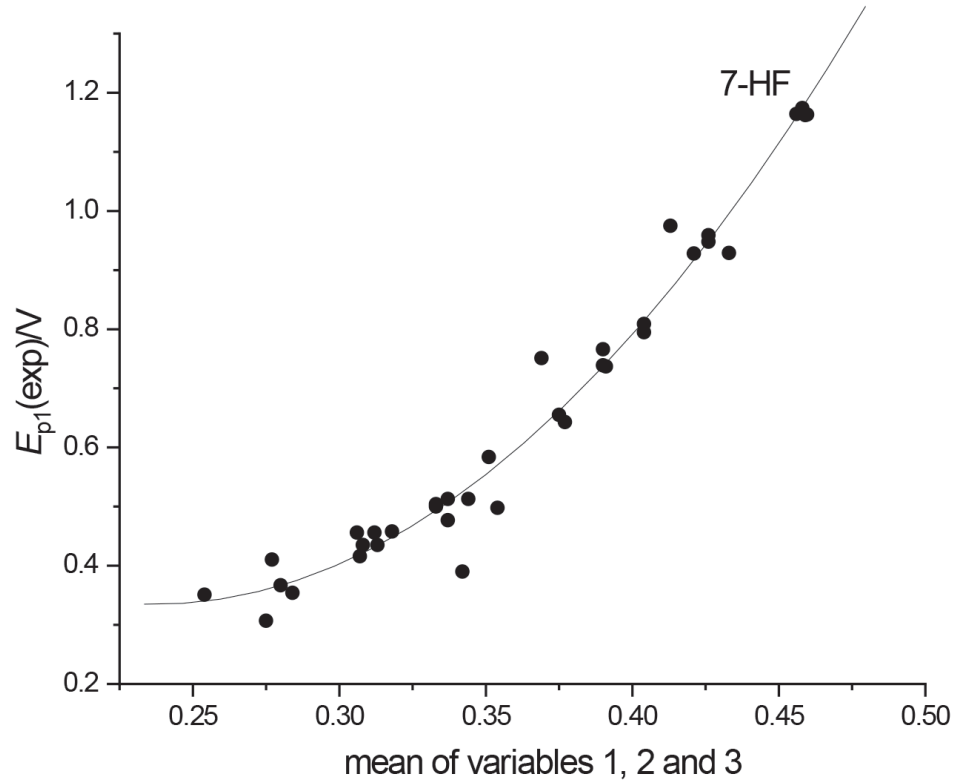

Figure 2 The dependence of experimental E_{p1} (pH=3) on the mean of $\sum_{s(C)} \Delta NAC_{Cat\text{-}Neut}$, $\sum_{s(C)} \Delta NAC_{Rad\text{-}Anion}$ and $\sum_{s(C)} \Delta NAC_{Rad\text{-}Neut}$ (variables 1, 2, and 3) for the set of 35 flavonoids published previously (1), with the addition of 7-HF