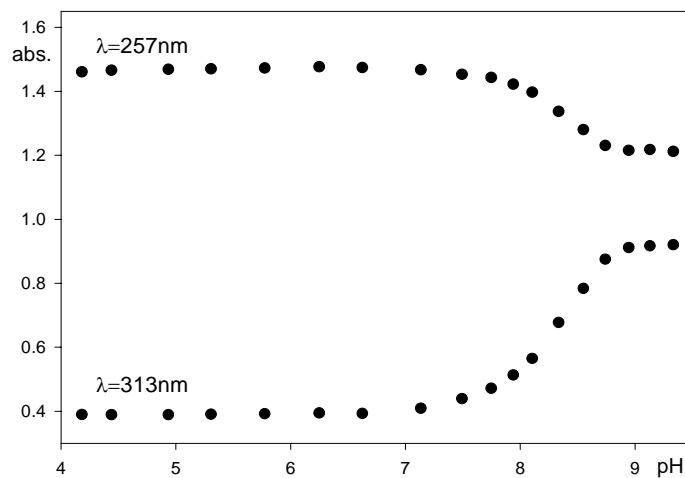
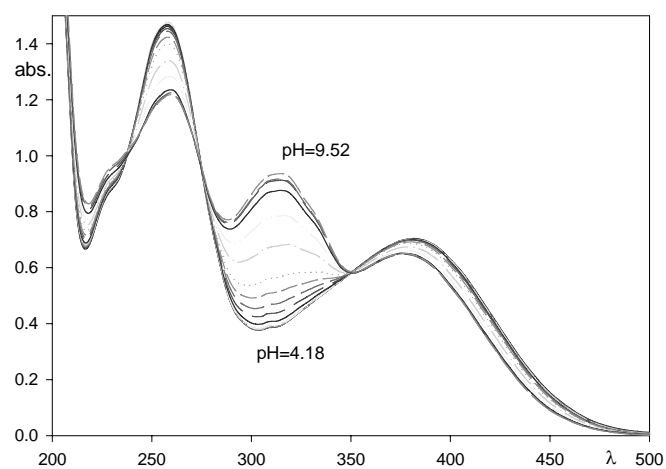
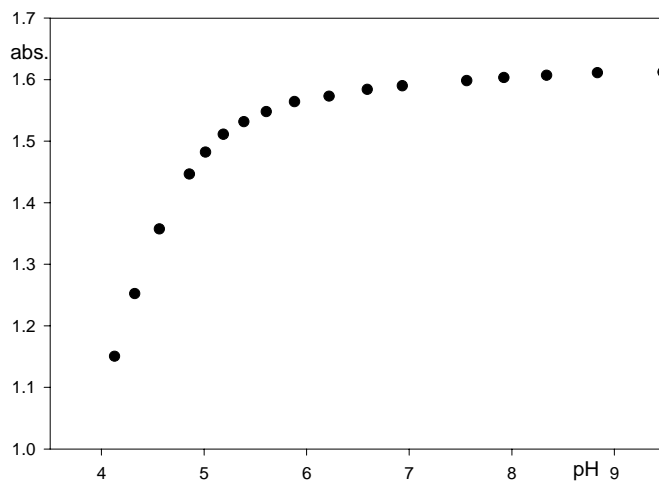
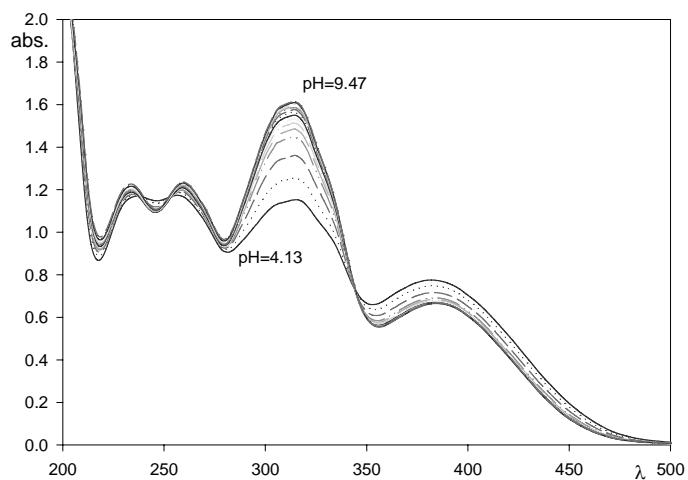


UV- Visible titration of norbadione A (**1**).



UV- Visible titration of pulvinic acid derivative **2**.



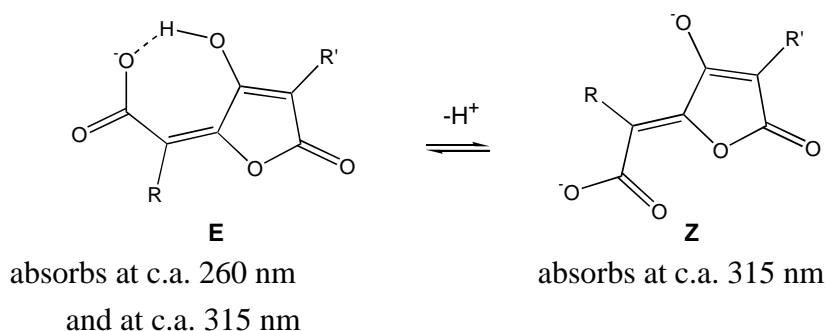
UV- Visible titration of pulvinic acid derivative **3**.

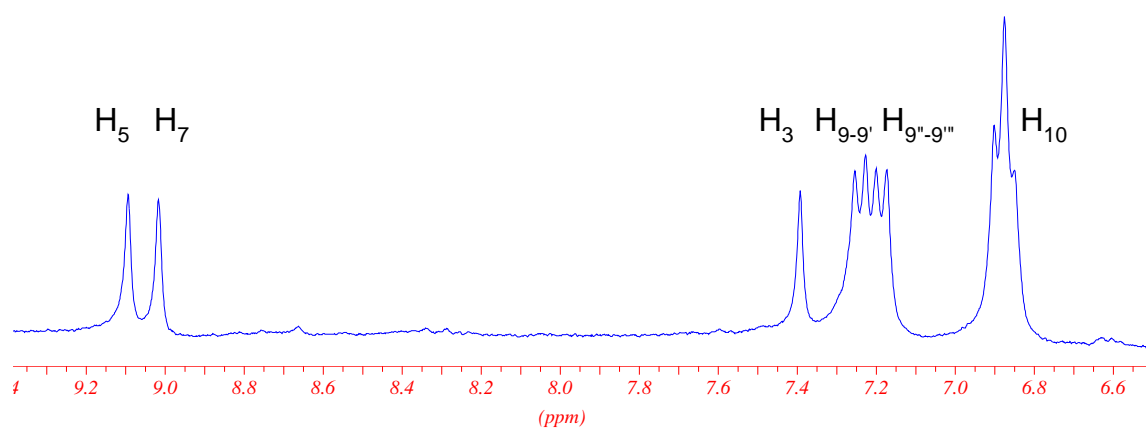
## Comments

- The characteristics of the absorption bands for the norbadione A, compound **2** and **3** are listed below.

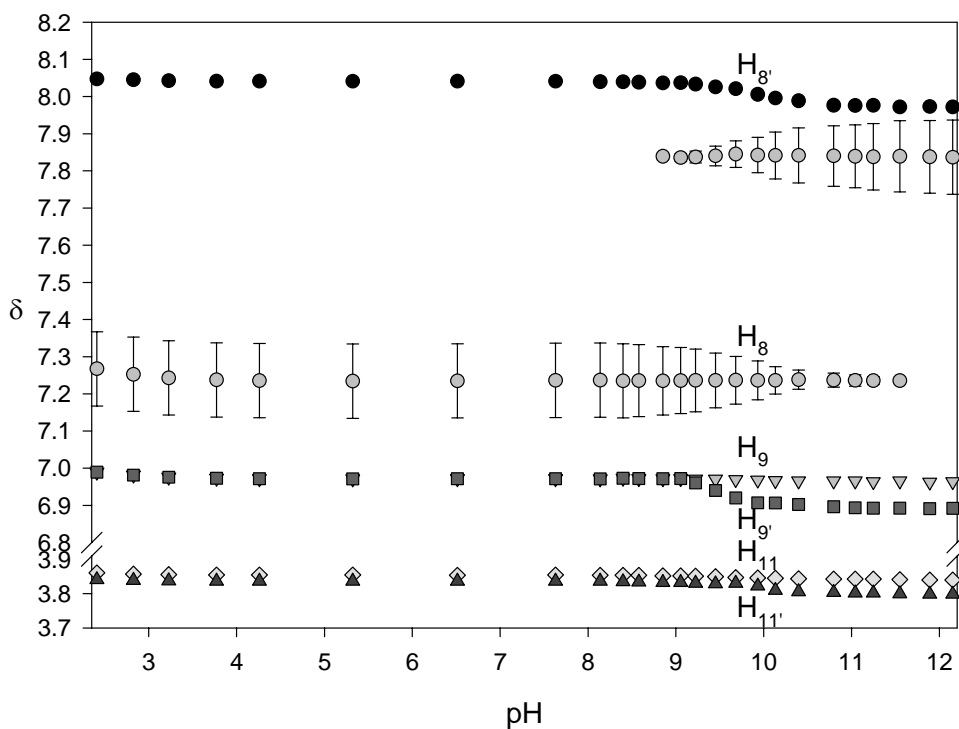
		$\epsilon \times 10^{-4} \text{ (M}^{-1} \text{ cm}^{-1}\text{)}$	
		pH=5.0	pH=9.1
(1)	$\lambda=230\text{nm}$	3.2	3.9
	$\lambda=267\text{nm}$	4.3	2.9
	$\lambda=315\text{nm}$	1.5	3.5
	$\lambda=485\text{nm}$	0.2	0.9
(2)	$\lambda=257\text{nm}$	4.6	3.8
	$\lambda=313\text{nm}$	1.2	2.9
(3)	$\lambda=257\text{nm}$	3.3	3.3
	$\lambda=313\text{nm}$	4.1	4.5

- It can be observed that, whereas, for norbadione A and compound **2**, there is an isobestic point and an increase of the band at about 260 nm by decreasing pH, there is no isobestic point for compound **3** and the absorption, at the contrary, decreases. Thus, it is concluded, that for norbadione A and compound **2**, which both possess the enol and carboxylate groups, the main absorption band at about 260 nm can be attributed to the protonated enol hydrogen bonded with the carboxylate group. Taking into account the structure of the molecules, intramolecular resonance-assisted O-H...O hydrogen bonding and  $\pi$ -delocalization confers a pseudo-aromatic character at this moiety which therefore absorbs at 267 nm or 258 nm. For compound **3**, the hydrogen bond is much weaker (also attested by the protonation constants), so that the species protonated at the enol group no longer absorbs at 258 nm. This can be summarized by the following scheme:

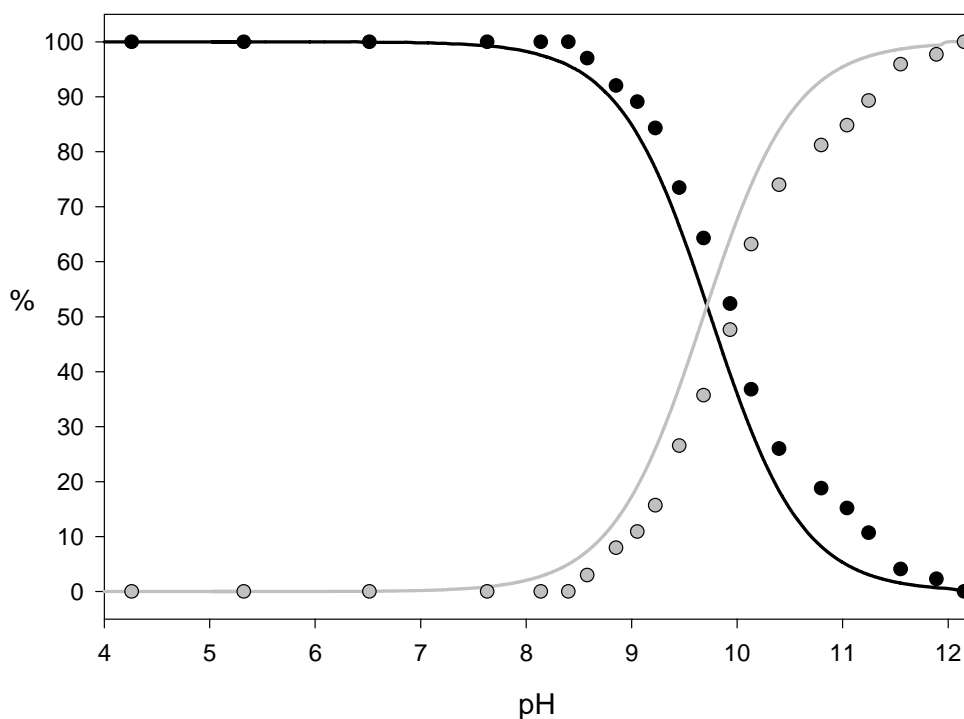




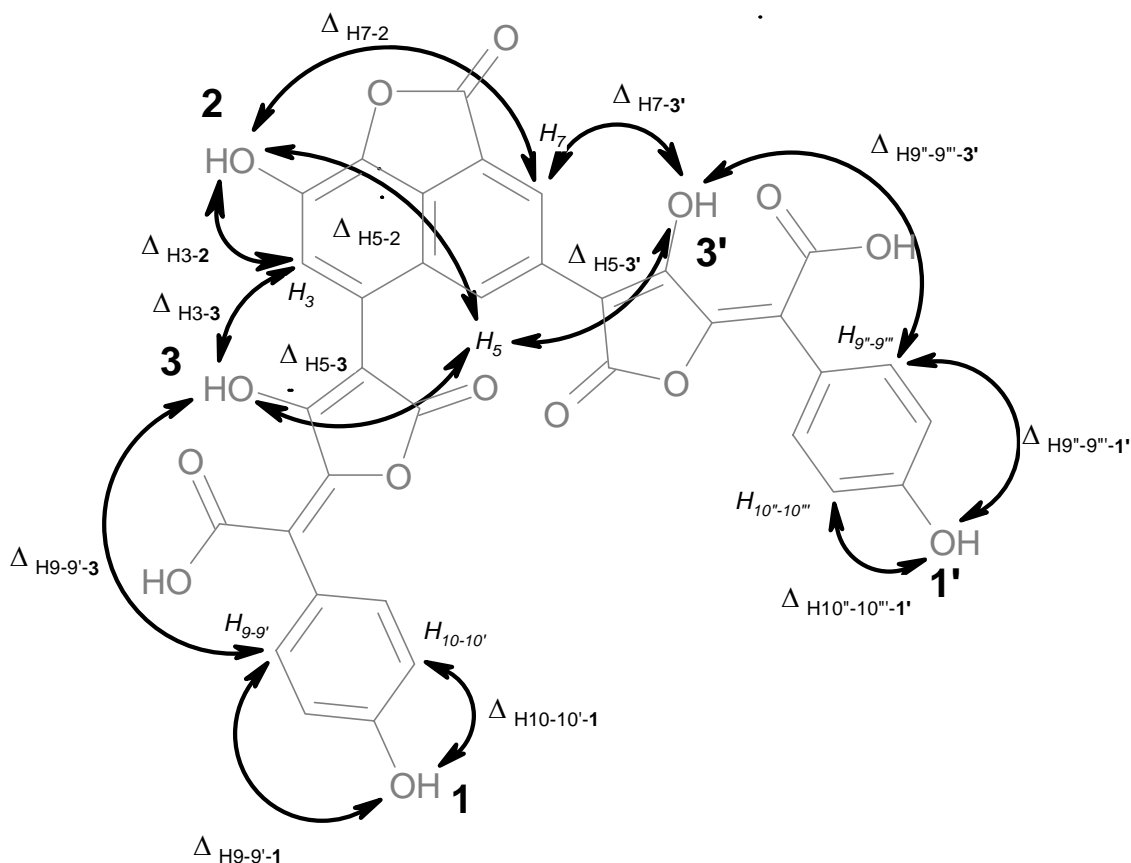
$^1\text{H}$ -NMR spectrum of norbadione A at pH 4.00 in  $\text{CD}_3\text{OD}:\text{D}_2\text{O}$ -80:20 at 25 °C



Titration curves of compound **2** in  $\text{CD}_3\text{OD}:\text{D}_2\text{O}$ -80:20 at  $-15^\circ\text{C}$ . The bar lengths result from the integration of the  $\text{H}_8$  peaks for both E and Z forms.



Black and grey lines correspond respectively to the percentages of protonated and deprotonated enol forms calculated with a  $\log K$  value of 9.75. This value results from the NMR curves displayed above performed at  $-15^\circ\text{C}$ . ● and ○ correspond respectively to the percentages of E and Z isomers. This clearly shows that deprotonation of the enol group triggers the E to Z isomerization.

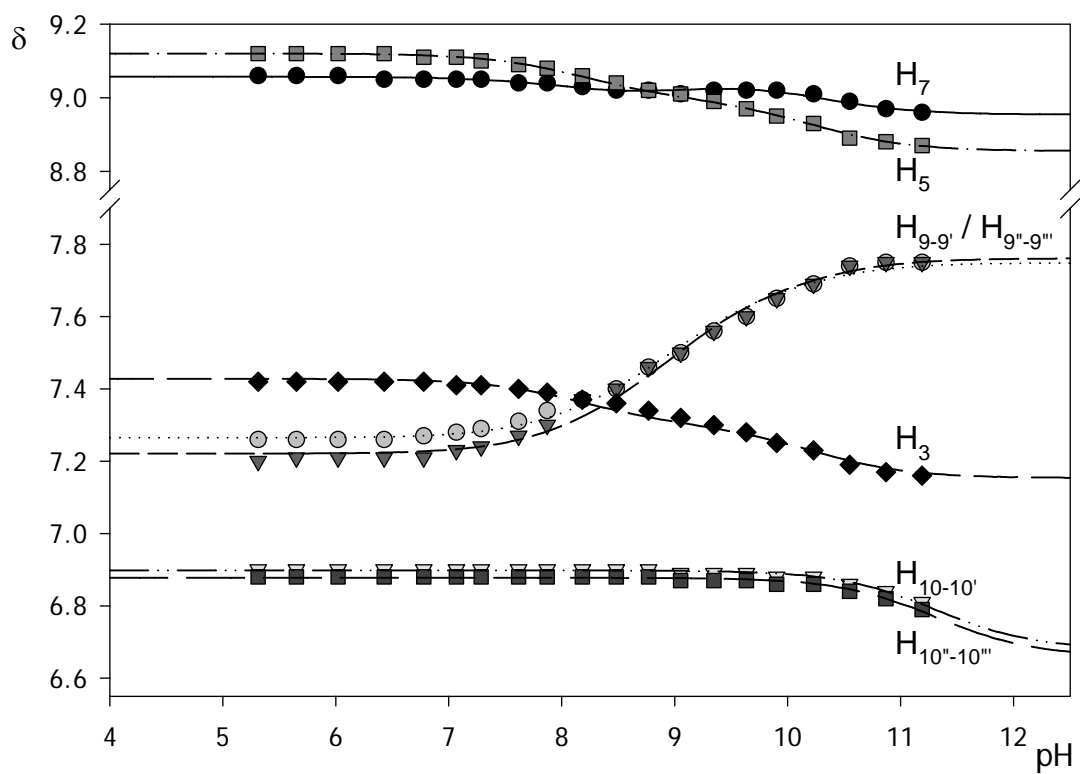


### norbadione A (1)

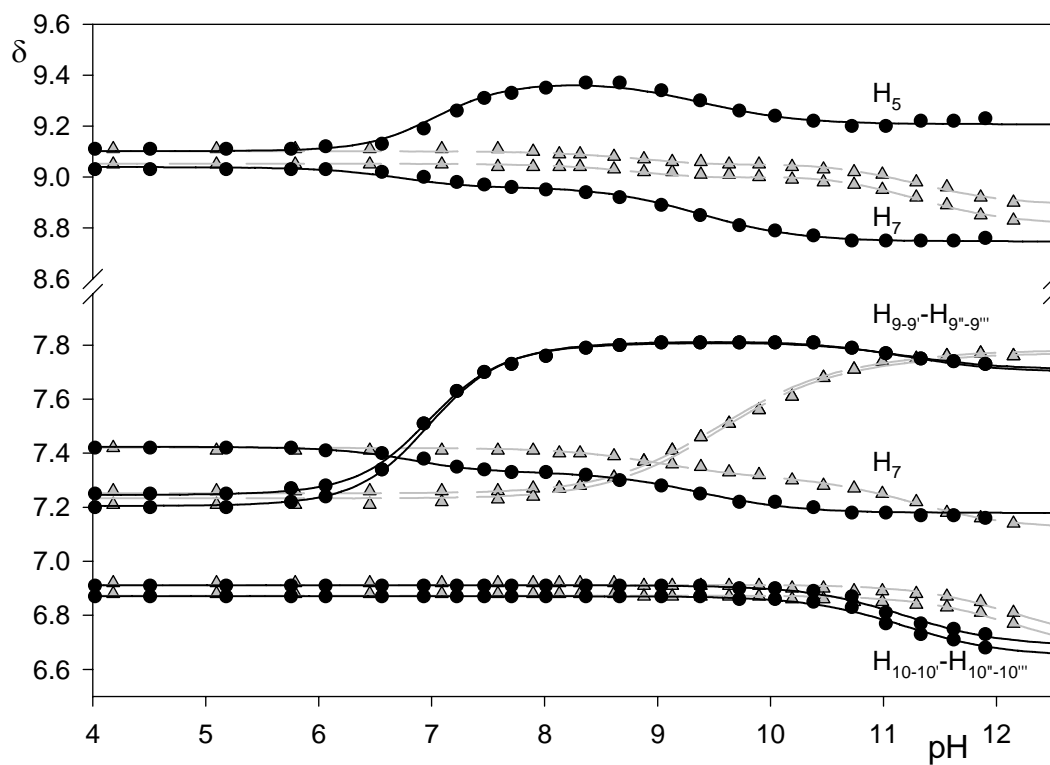
Calculations by Borkovec's program in CD<sub>3</sub>OD:D<sub>2</sub>O-80:20

$\Delta\delta$ (ppm)	without salt	Et <sub>4</sub> NClO <sub>4</sub> 0.1M	NaCl 0.15M	
$\Delta_{H7-2}$	0.2463	0.2616	0.1536	0.2202
$\Delta_{H7-3'}$	/	-0.0229	-0.0509	0.0716
$\Delta_{H3-2}$	0.2920	0.2232	0.1842	0.1542
$\Delta_{H3-3}$	/	0.0739	0.0903	0.0910
$\Delta_{H5-2}$	0.2146	0.2183	0.1750	0.1828
$\Delta_{H5-3'}$	/	-0.0229	-0.0509	0.0716
$\Delta_{H5-3}$	/	0.0165	0.1411	-0.3599
$\Delta_{H9-9'-3}$	-0.5298	-0.5294	-0.4840	-0.5672
$\Delta_{H9-9'-1}$	/	/	/	0.1028
$\Delta_{H9''-9'''-3'}$	-0.5381	-0.5377	-0.5403	-0.6129
$\Delta_{H9''-9'''-1'}$	/	/	/	0.1176
$\Delta_{H10-10'-1}$	0.2134	0.2134	0.2178	0.2247
$\Delta_{H10''-10'''-1'}$	0.2134	0.2134	0.2178	0.2247

Chemical shift parameters



Titration curves of norbadione A (1) in  $\text{Et}_4\text{NClO}_4$  0.10 M at  $25^\circ\text{C}$



Superimposition of the titration curves performed without supporting-electrolyte (in grey) and in NaCl 0.15 M (in black)