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Type of the Paper (Article)

Application of screen printed diamond electrode, coupled with "point-of-care" platform, for nanomolar quantification of phyto-nutrient pterostilbene in dietary supplements. An experimental study supported by theory

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Supplementary material

Figures

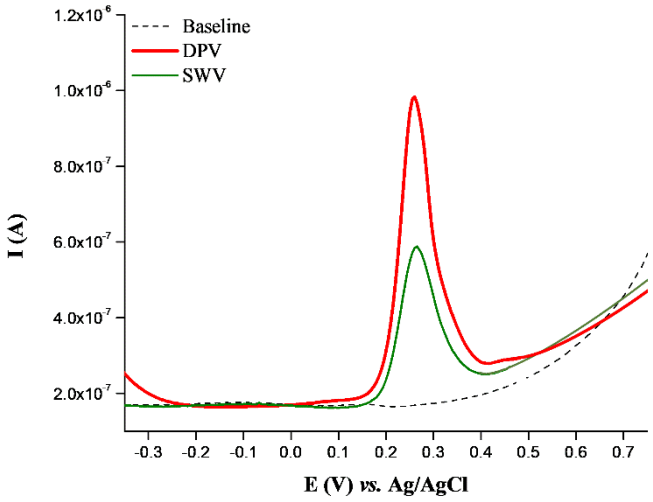

Figure S1. Electrochemical response of 6 μmol L^{-1} PTS in BRBS (pH=9) at SPDE recorder by DPV (modulation amplitude 25 mV; modulation time 0.05 s; interval time 0.5 s) and SWV (modulation amplitude 20 mV; frequency 25 Hz).

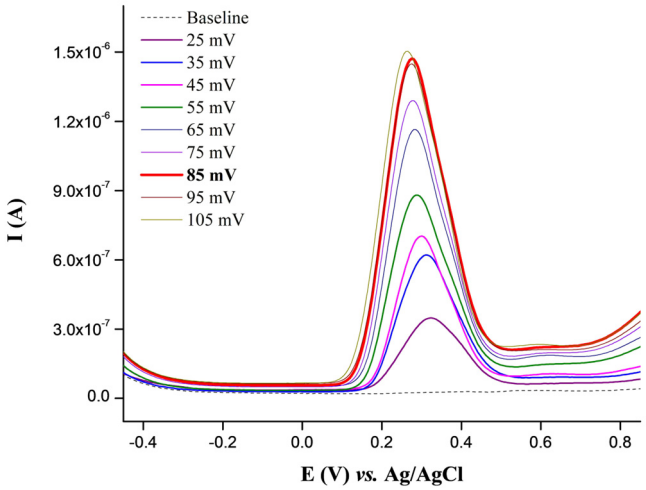

Figure S2. DP voltammograms for 0.65 μmol L^{-1} of PTS in BRBS (pH=9) recorder at different modulation amplitudes (modulation time of 50 ms; interval time of 500 ms).

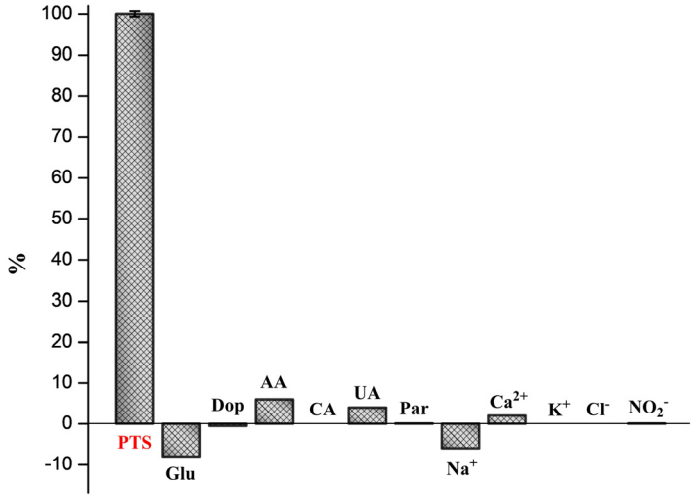

Figure S3. Effect of possible interfering compounds for the detection of PTS by SPDE. All experiments were done under previously optimized experimental conditions (the optimized DPV parameters: modulation amplitude of 85 mV; modulation time of 50 ms; interval time of 500 ms).

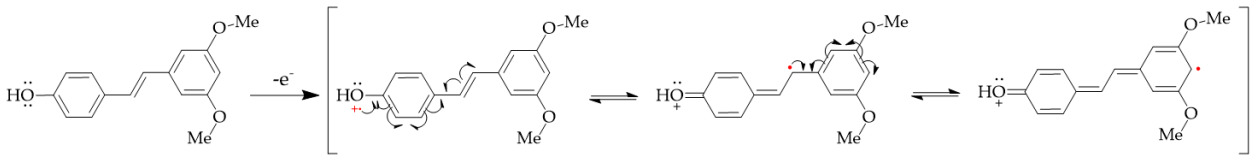

Figure S4. Possible resonance hybrid-structures, generated after the oxidation of phenol OH- group.

Tables

Table S1. Mulliken charge analysis and calculated Fukui functions for PTS and corresponding oxidized adduct

		[PTS]						[PTS]$^+$						
No.	A.	N	N+1	N-1	*Nu.*	*El.*	*Rad.*	N	N+1	N-1	*Nu.*	*El.*	*Rad.*	*Spin-Density*
1	O	-0.332	-0.348	-0.318	-0.02	-0.01	-0.01	-0.318	-0.330	-0.299	-0.01	-0.02	-0.02	-0.006
2	O	-0.333	-0.346	-0.317	-0.01	-0.02	-0.01	-0.316	-0.331	-0.293	-0.01	-0.02	-0.02	0.003
3	O	-0.476	-0.508	-0.408	-0.03	-0.07	-0.05	-0.385	-0.453	-0.316	-0.07	-0.07	-0.07	0.075
4	C	0.197	0.175	0.211	-0.02	-0.01	-0.02	0.198	0.189	0.233	-0.01	-0.03	-0.02	0.000
5	C	-0.416	-0.492	-0.377	-0.08	-0.04	-0.06	-0.384	-0.425	-0.339	-0.04	-0.05	-0.04	0.058
6	C	-0.363	-0.422	-0.302	-0.06	-0.06	-0.06	-0.301	-0.364	-0.236	-0.06	-0.06	-0.06	0.122
7	C	0.378	0.374	0.373	0.00	0.01	0.00	0.371	0.377	0.371	0.01	0.00	0.00	-0.047
8	C	0.340	0.344	0.340	0.00	0.00	0.00	0.334	0.336	0.337	0.00	0.00	0.00	-0.039
9	C	-0.176	-0.293	-0.068	**-0.12**	**-0.11**	**-0.11**	-0.058	-0.173	0.028	**-0.12**	**-0.09**	**-0.10**	***0.218***
10	C	0.165	0.161	0.226	0.00	-0.06	-0.03	0.218	0.157	0.287	-0.06	-0.07	-0.07	0.114
11	C	-0.364	-0.456	-0.275	**-0.09**	**-0.09**	**-0.09**	-0.281	-0.370	-0.176	**-0.09**	**-0.10**	**-0.10**	***0.190***
12	C	-0.181	-0.323	-0.106	**-0.14**	-0.08	**-0.11**	-0.104	-0.174	-0.051	-0.07	-0.05	-0.06	0.096
13	C	-0.236	-0.326	-0.194	**-0.09**	-0.04	-0.07	-0.194	-0.237	-0.161	-0.04	-0.03	-0.04	0.057
14	C	-0.199	-0.238	-0.161	-0.04	-0.04	-0.04	-0.159	-0.198	-0.128	-0.04	-0.03	-0.04	0.046
15	C	-0.233	-0.248	-0.190	-0.02	-0.04	-0.03	-0.196	-0.240	-0.155	-0.04	-0.04	-0.04	-0.006
16	C	-0.252	-0.276	-0.210	-0.02	-0.04	-0.03	-0.209	-0.253	-0.171	-0.04	-0.04	-0.04	0.008
17	C	0.305	0.261	0.354	-0.04	-0.05	-0.05	0.359	0.308	0.408	-0.05	-0.05	-0.05	***0.144***
18	C	-0.202	-0.197	-0.208	0.01	0.01	0.01	-0.206	-0.201	-0.213	0.01	0.01	0.01	0.000
19	C	-0.206	-0.199	-0.210	0.01	0.00	0.01	-0.210	-0.206	-0.214	0.00	0.00	0.00	0.000

Table S2. HOMO LUMO energy of PTS and PTSH+ and corresponding HOMO-LUMO gap

Structure	HOMO		LUMO		*LUMO-HOMO*	
	eV	Kcal/mol	eV	Kcal/mol	eV	Kcal/mol
PTS	-5.4	-125.2	-1.5	-33.5	4.0	91.7
PTSH+	-5.8	-134.6	-1.8	-41.0	4.1	93.7

All theoretical results presented in this work are obtained trough Orca [S1] electronic structure program suite (Program Version 5.0.2), by using Density Functional Theory (DFT) [S2,S3] approach. All calculations have been carried out on B3LYP [S4,S5] level of theory, coupled with def2-TZVP orbital basis set with the dispersion correction on the D3BJ-level [S6]. To make calculations as realistic as possible, solvation effects of water have been included using the conductor-like polarizable continuum model (C-PCM) [S7]. Table S1 contain Mulliken charge analysis information [8,9], together with the condensed forms of the Fukui functions [S10-S12], for all investigated molecular species in this work. All molecules have been fully optimized in the framework of described computational conditions. Orbital analysis was systematically undertaken to view the localization of the

unpaired electrons (where present). Specific molecule of interest is emphasized in the caption of the Table, together with its fully optimized one-electron oxidized analogue (corresponding field below). N stands for the emphasized molecule, and N+1 and N-1 represent corresponding nonoptimized, anionic and cationic form of that specific molecule (example: Table S1. N: $[PTS]^0$ N+1: $[PTS]^-$ N-1: $[PTS]^+$). Abbreviations *Nu. El.* and *Rad.* represent reactivity towards nucleophiles, electrophiles and radical species respectively. Hydrogen atoms are not shown (since they are not relevant for the study), and most important values for remaining heavy atoms are indicated by bold formatting for better understanding.

The condensed forms of the Fukui function for an atom j in a specific molecule, are calculated using the equations 1, 2 and 3, for a nucleophilic $\left(\boldsymbol{f_j^+(r)}\right)$, electrophilic $\left(\boldsymbol{f_j^-(r)}\right)$, and radical attack $\left(\boldsymbol{f_j^0(r)}\right)$, respectively. In these equations q_j is the atomic charge, evaluated from the Mulliken charge analysis, at the j_{th} atomic site in the neutral (*N*), anionic (*N+1*), or cationic (*N-1*) chemical species.

$$f_j^+(r) = q_{j(N)} - q_{j(N+1)}, \quad (1)$$

$$f_j^-(r) = q_{j(N-1)} - q_{j(N)}, \quad (2)$$

$$f_j^0(r) = \frac{1}{2}\{q_{j(N-1)} - q_{j(N+1)}\} \quad (3)$$

XYZ coordinates of PTS

O	-4.274045000	-2.234112000	0.002692000
O	-3.695839000	2.494037000	0.034140000
O	6.775898000	-0.516046000	-0.033988000
C	-1.227148000	-0.255078000	0.016322000
C	-1.736187000	1.058174000	0.024790000
C	-2.113804000	-1.329919000	0.009967000
C	-3.493929000	-1.110054000	0.010359000
C	-3.106648000	1.257367000	0.025674000
C	0.205414000	-0.545370000	0.012855000
C	2.633024000	0.071974000	-0.003879000
C	-4.003105000	0.179609000	0.018072000
C	1.201671000	0.355103000	0.002065000
C	3.168678000	-1.225520000	0.014745000
C	3.537404000	1.143846000	-0.030651000
C	4.535691000	-1.439827000	0.005444000
C	4.909104000	0.942691000	-0.040635000
C	5.412089000	-0.354239000	-0.023076000
C	-5.692731000	-2.066915000	-0.000399000
C	-2.846455000	3.642364000	0.042823000
H	-1.062699000	1.899910000	0.031218000
H	-1.742679000	-2.346660000	0.003678000
H	0.447173000	-1.602944000	0.017380000
H	-5.063043000	0.383255000	0.018856000
H	0.957000000	1.412315000	-0.005495000
H	2.511503000	-2.084782000	0.037085000
H	3.151152000	2.155990000	-0.044789000
H	4.933679000	-2.447701000	0.020127000
H	5.593841000	1.780722000	-0.062056000
H	-6.110744000	-3.070721000	-0.007721000
H	-6.022370000	-1.527542000	-0.891228000
H	-6.027612000	-1.538297000	0.894869000
H	-2.217242000	3.659477000	0.935421000
H	-3.511273000	4.502901000	0.050383000
H	-2.218824000	3.673920000	-0.850510000
H	6.992855000	-1.459229000	-0.025935000

XYZ coordinates of $PTSH^+$

O	-4.252627000	-2.239854000	-0.014772000
O	-3.706293000	2.490448000	0.083075000
O	6.780631000	-0.570496000	-0.146637000
C	-1.221753000	-0.240099000	0.012931000
C	-1.736347000	1.069882000	0.041753000
C	-2.098310000	-1.322047000	-0.002169000
C	-3.480196000	-1.111889000	0.005101000
C	-3.108204000	1.259648000	0.051446000
C	0.212216000	-0.522210000	-0.001568000
C	2.634054000	0.090061000	-0.061061000
C	-3.995984000	0.174733000	0.031613000
C	1.202451000	0.381767000	-0.048860000
C	3.155920000	-1.210276000	0.023951000
C	3.535345000	1.160231000	-0.159024000
C	4.522576000	-1.436243000	0.013437000
C	4.908549000	0.956409000	-0.179648000
C	5.353646000	-0.341714000	-0.087015000
C	-5.672810000	-2.081604000	-0.016350000
C	-2.865534000	3.645460000	0.103558000
H	-1.067218000	1.914899000	0.060408000
H	-1.718678000	-2.335331000	-0.022646000
H	0.458495000	-1.578089000	0.023657000
H	-5.057326000	0.371090000	0.039673000
H	0.959897000	1.437948000	-0.087160000
H	2.496518000	-2.062520000	0.106677000
H	3.152988000	2.170569000	-0.224180000
H	4.928695000	-2.436933000	0.085242000
H	5.603870000	1.781000000	-0.260707000
H	-6.084072000	-3.087909000	-0.037680000
H	-6.004928000	-1.532100000	-0.900007000
H	-6.011070000	-1.567194000	0.885806000
H	-2.231647000	3.654248000	0.992940000
H	-3.537180000	4.500291000	0.127134000
H	-2.243310000	3.694194000	-0.792685000
H	7.043201000	-1.485801000	0.083653000
H	7.309203000	0.061363000	0.384721000

Author Contributions: conceptualization, investigation, methodology, supervision, writing-original draft preparation, visualization, **S.Đ.**; investigation, writing-original draft preparation, visualization, **F.V.**; investigation, formal analysis, **M.M.**; validation, **J.M.**; formal analysis, **D.M.**; investigation, validation, **V.S.**; writing-review and editing, visualization, **Ľ.Š.**; investigation, methodology writing-review and editing, visualization, supervision, project administration, funding acquisition, **D.S. All authors have read and agreed to the published version of the manuscript.**

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