Electronic Supplementary Material (ESI) for Food & Function.

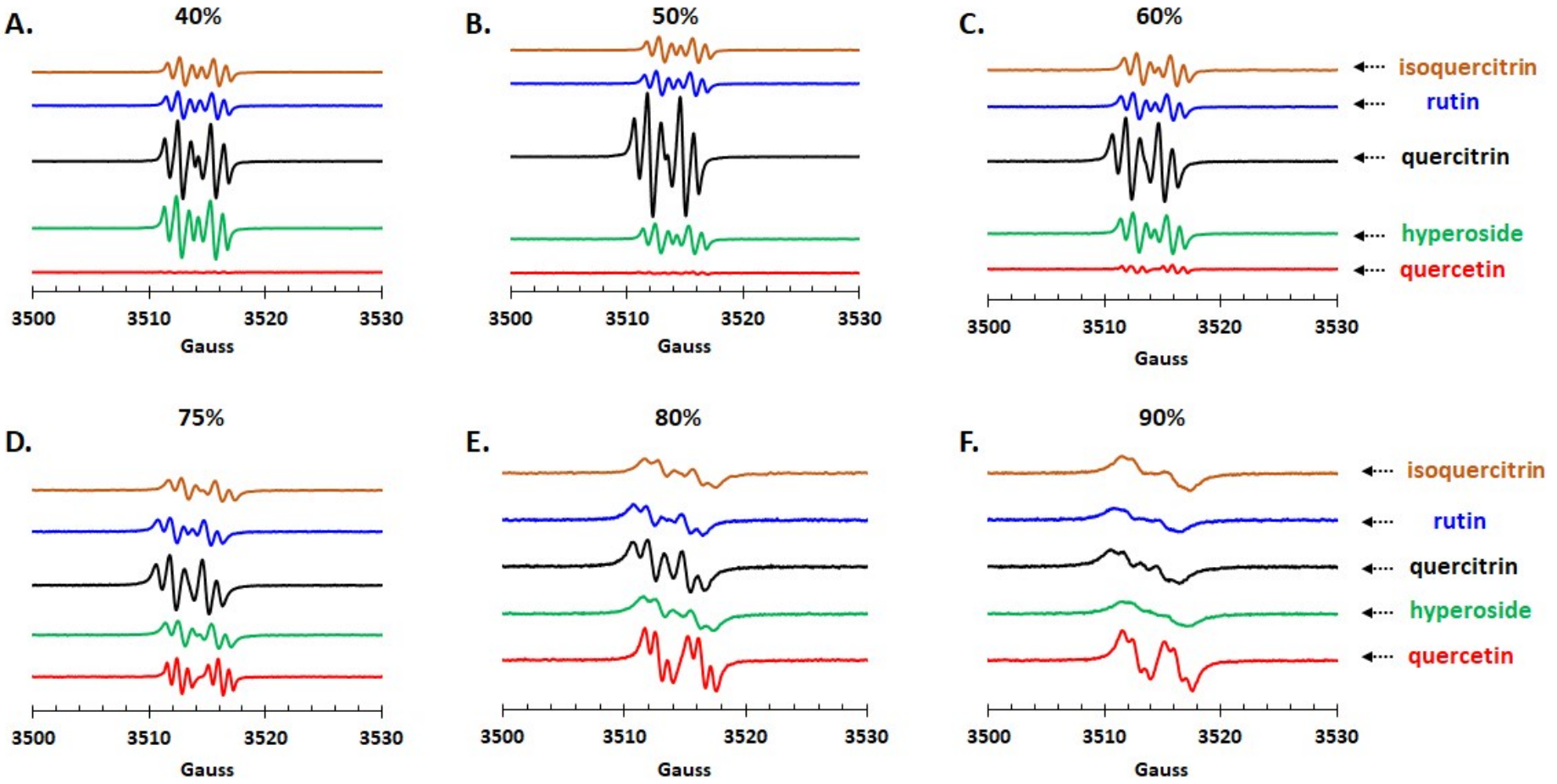

Figure S1. *X-band EPR spectra of the semiquinone anion radicals of the quercetin and its studied glycosides (1 mM), at room temperature in water-methanol solution at different methanol content (indicated in volume %).*

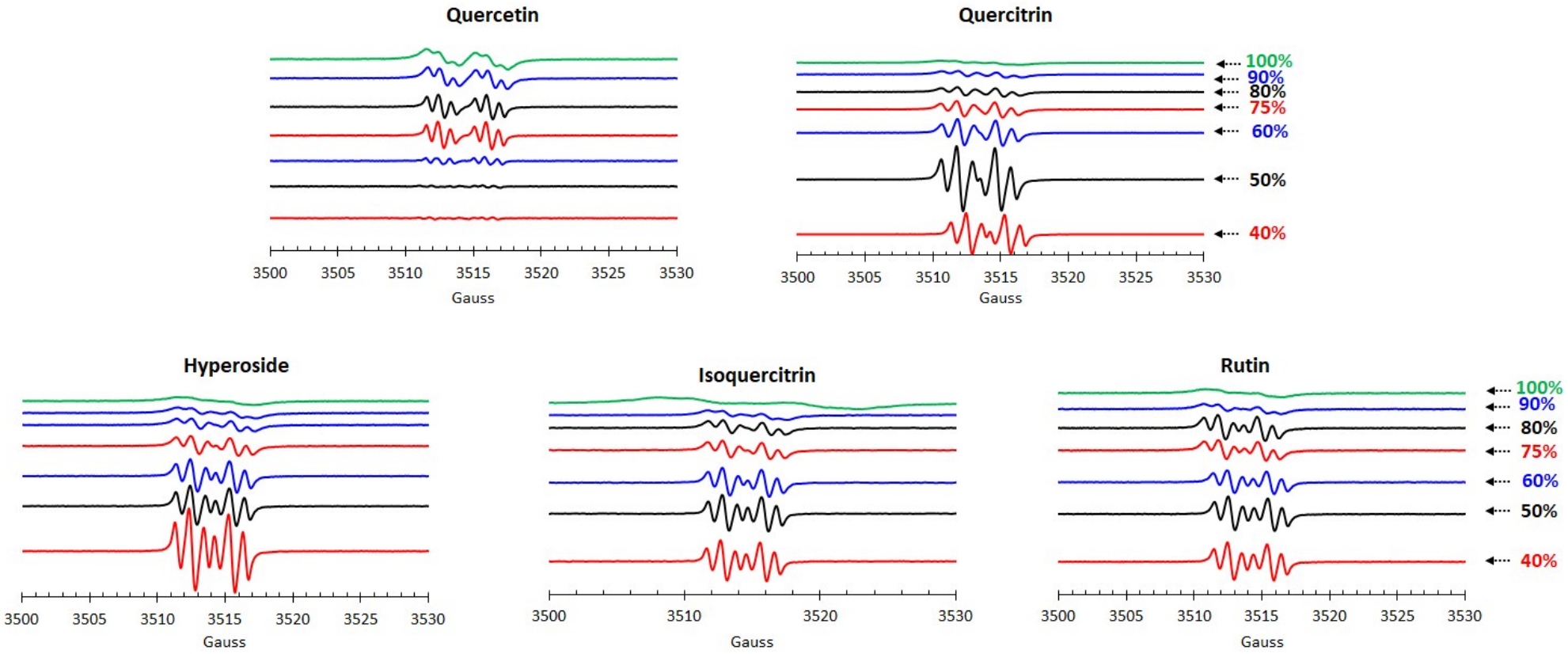

Figure S2. *X-band EPR spectra of the semiquinone anion radicals of the quercetin and its studied glycosides (1 mM), at room temperature in water-methanol, arranged as to emphasize linewidth and hyperfine coupling constants evolution as methanol concentration dependence.*

Table S1. *Hyperfine coupling constants (a_{Hn}) of the three protons (see Figure 3 in main text) and linewidth (LW) for quercetin and its glycosides as function of methanol content. The values are determined from the experimental spectra using WinSim software.*

%MeOH (in water)	Sample name	g value	measured in Gauss			
			a_{H1}	a_{H2}	a_{H3}	LW
40	Quercetin	2.0049	3.0776	0.7880	1.4992	0.3848
50		2.0047	3.2040	0.8000	1.4328	0.3512
60		2.0048	3.5120	0.7504	0.9800	0.2816
75		2.0049	3.5280	0.7728	0.9408	0.2656
80		2.0049	3.5216	0.7888	0.9672	0.3032
90		2.0049	3.5144	0.7560	1.0656	0.5048
100		2.0048	3.4344	0.7656	1.1320	0.7400
40	Hyperoside	2.0050	2.8848	1.1320	0.9576	0.3280
50		2.0050	2.8672	1.1568	0.9728	0.3536
60		2.0050	2.8624	1.1704	0.9736	0.3816
75		2.0050	2.8616	1.2208	0.9856	0.5496
80		2.0048	2.8608	1.2560	0.9904	0.6800
90		2.0049	2.7952	1.3104	1.1008	0.8112
100		2.0049	2.6936	1.2632	0.8872	1.3656
40	Quercitrin	2.0050	2.8416	1.0720	1.1544	0.3032
50		2.0050	2.8336	1.1040	1.1264	0.3112
60		2.0050	2.8168	1.1016	1.2192	0.4312
75		2.0049	2.8136	1.1128	1.2160	0.4752
80		2.0050	2.8040	1.0920	1.2544	0.5280
90		2.0050	2.7880	1.0584	1.3560	0.6280
100		2.0050	2.8160	1.1520	1.2880	1.0808
40	Rutin	2.0050	2.8984	1.0872	0.9408	0.3568
50		2.0049	2.8936	1.1032	0.9400	0.3824
60		2.0050	2.8840	1.1464	0.9464	0.4272
75		2.0050	2.8984	1.1944	0.9344	0.4616
80		2.0050	2.8752	1.1528	0.9384	0.4040
90		2.0050	2.9096	1.1984	1.0008	0.8080
100		2.0050	2.7464	1.2568	0.8088	1.2280
40	Isoquercitrin	2.0050	2.8928	0.9592	1.1408	0.2824
50		2.0050	2.8848	0.9656	1.1792	0.3296
60		2.0050	2.8616	0.9808	1.1992	0.4008
75		2.0050	2.8624	0.9904	1.2352	0.4424
80		2.0050	2.8072	1.0064	1.3248	0.5648
90		2.0050	2.8416	0.9744	1.2288	1.0472
100		2.0049	2.7616	0.8208	1.2656	1.3104

Table S2. *Numerically computed parameters as described in main text. Hyperfine coupling constants (a_{Hn}) in G.*

Compound	Torsion angle*	a_{H1}	a_{H2}	a_{H3}
Quercetin	-	4.188	0.738	0.927
Isoquercitrin	-18.2	1.980	1.732	0.939
Hyperoside	18.6	2.395	1.553	0.653
Quercitrin	-26.8	2.848	1.202	2.047
Rutin	-34	1.514	0.668	0.634

*as determined from the optimised structures shown in Figure 5 (main text).

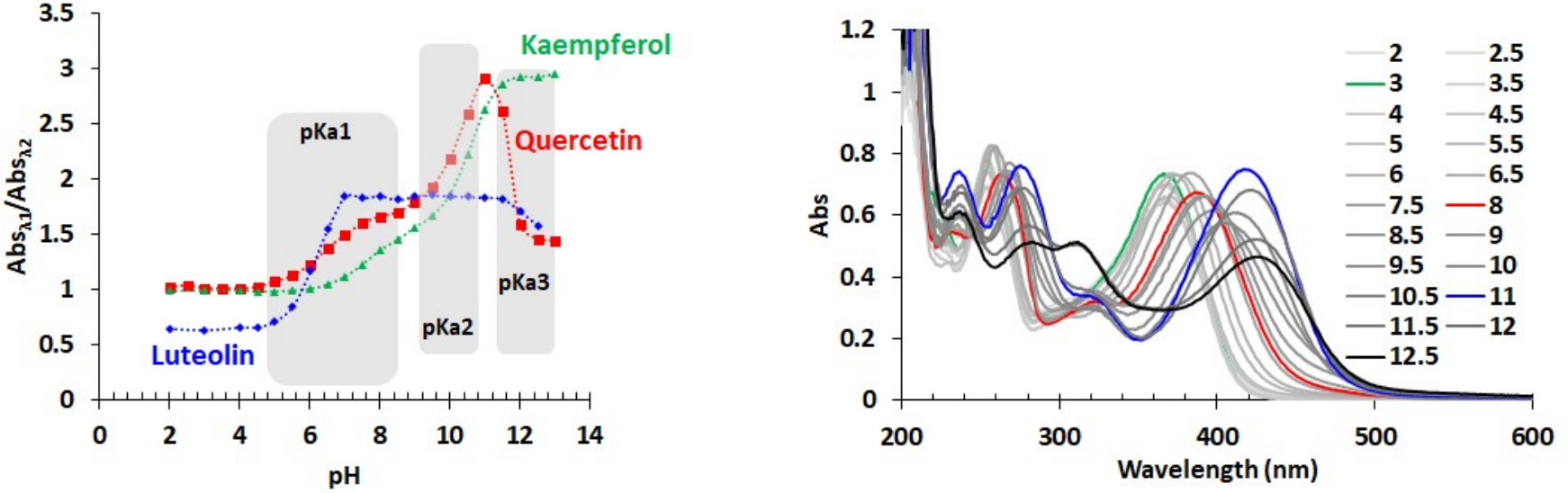

Figure S3. ***Left****: Titration curves for quercetin, kaempferol and luteolin used for pKa determination.* ***Right****: Illustrative spectral changes of quercetin obtained in pH titration.*

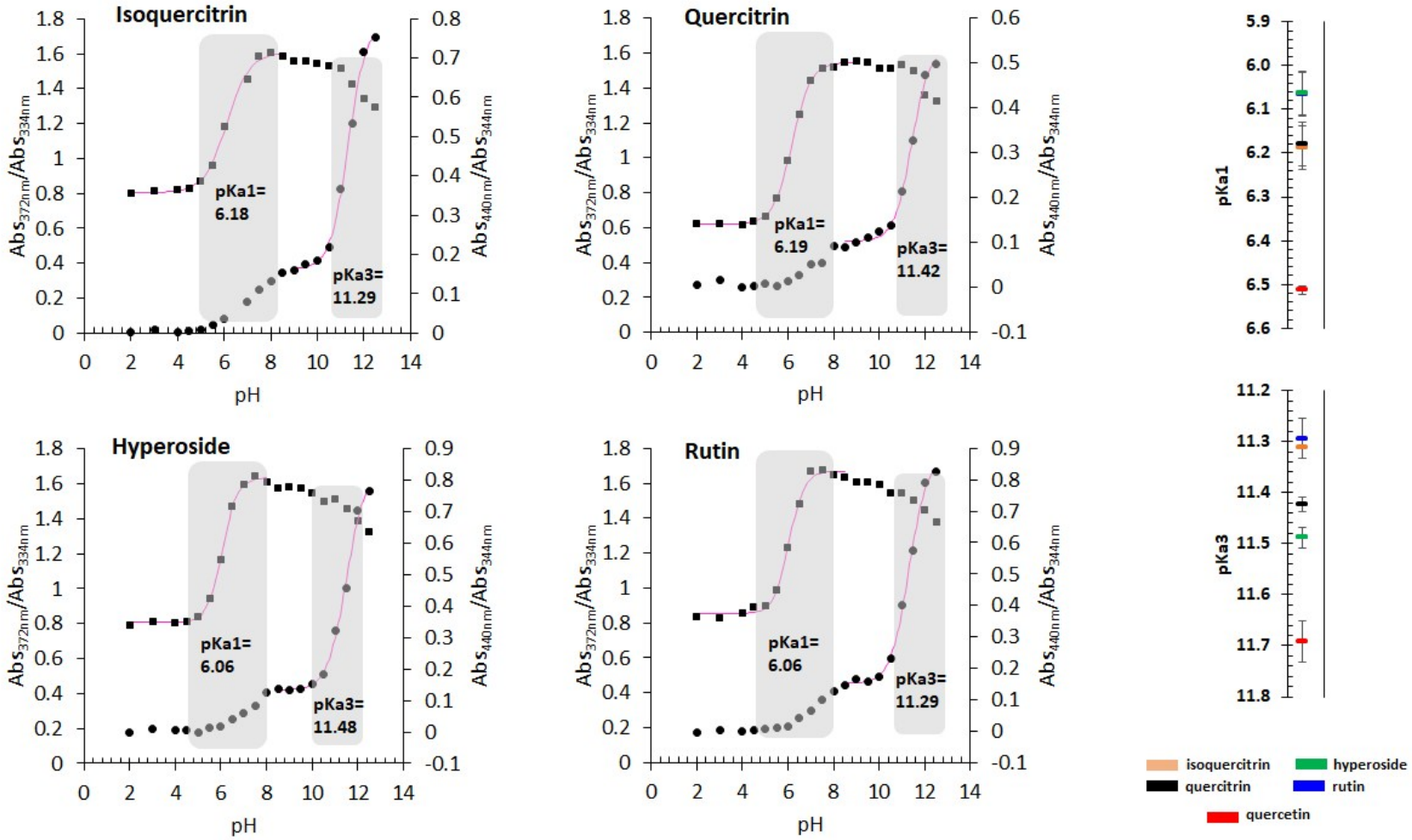

Figure S4. *pKa determination using pH titration via molecular absorption spectrophotometry following their spectral profile change at the indicated wavelengths – full circles indicating the ratio of the absorbances in the right axis title and squares indicating the ratio of the absorbances in the left axis title. The pKa values were determined after applying a sigmodal function for fitting (fitting curves indicated in magenta).*

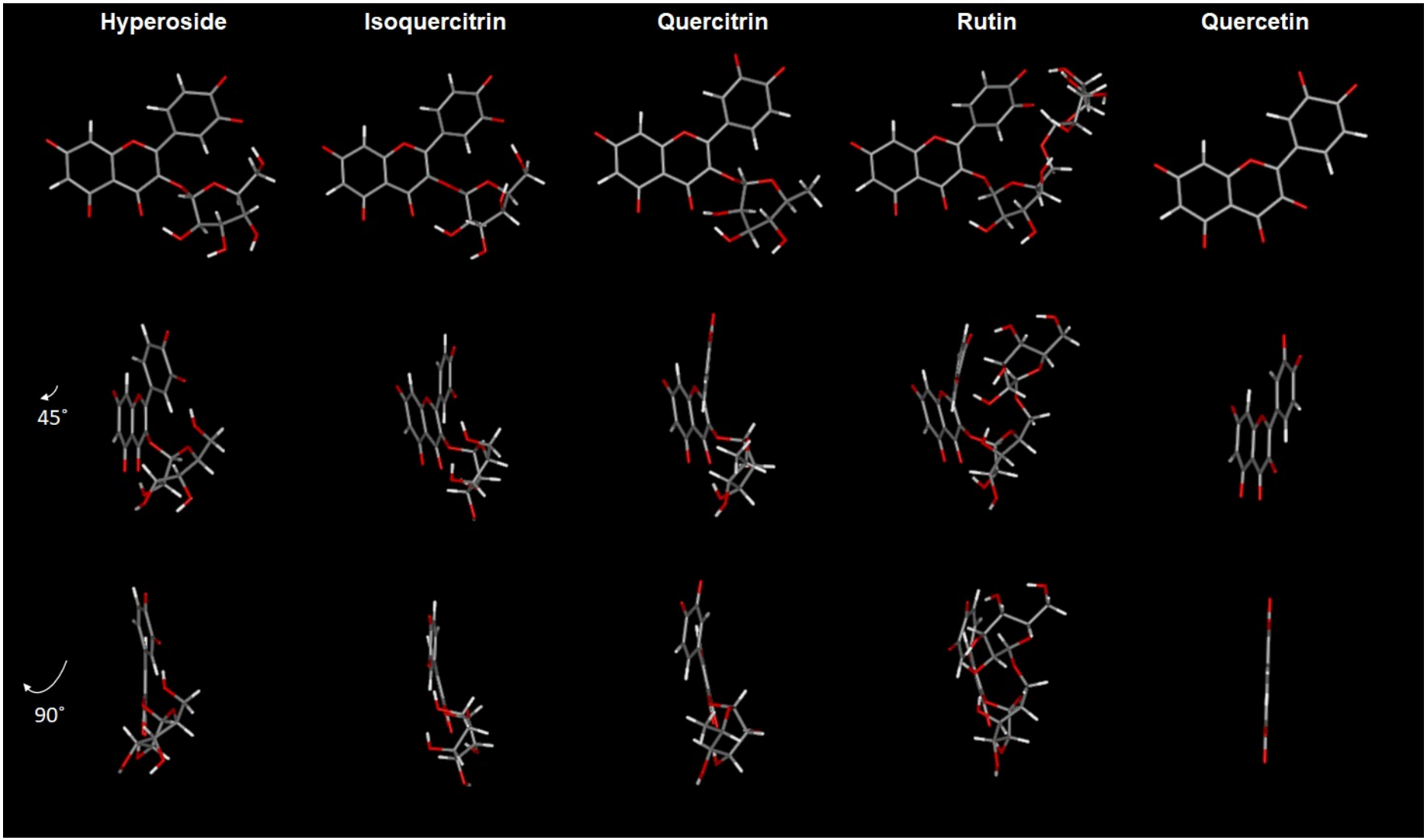

Figure S5. *Modelled structures of studied compounds, in completed deprotonated state presented in three perspectives.*

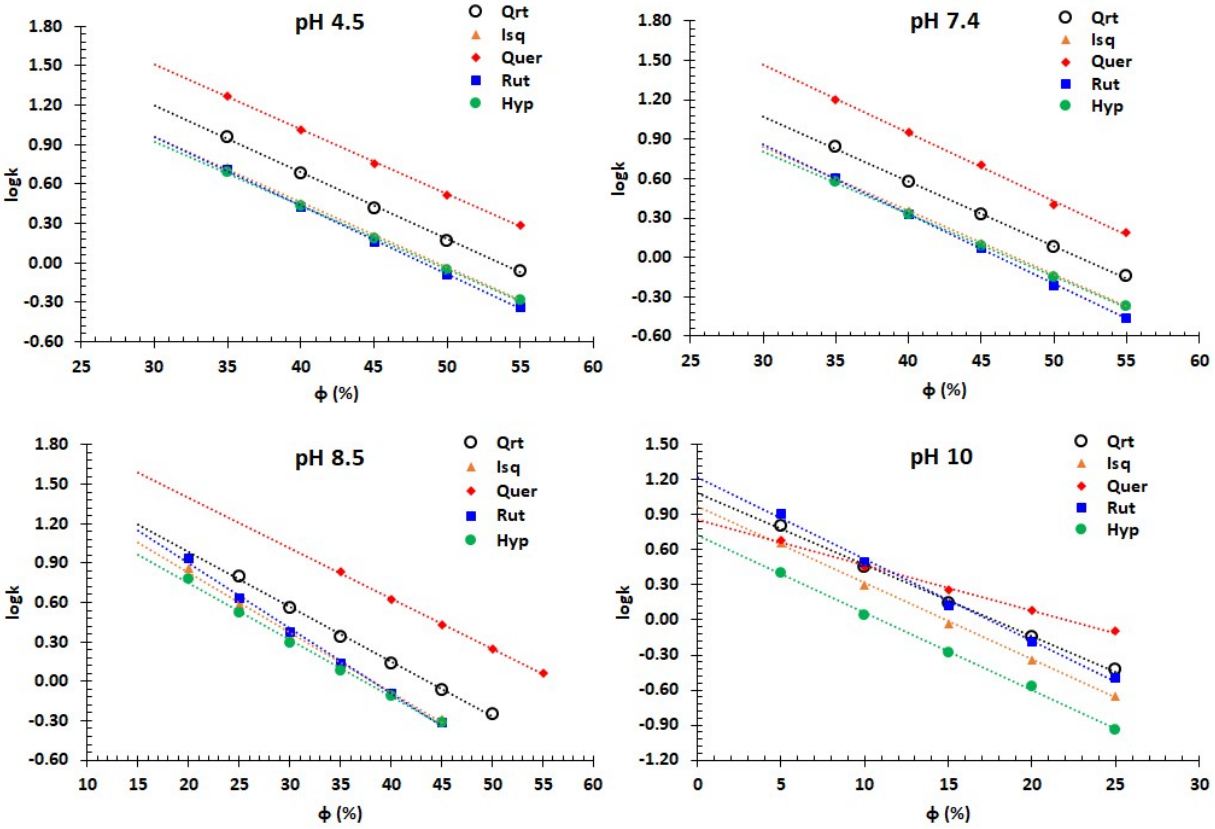

Figure S6. *Lipophilicity determination from logk linear dependence on methanol content () in isocratic HPLC approach as described in the main text.*

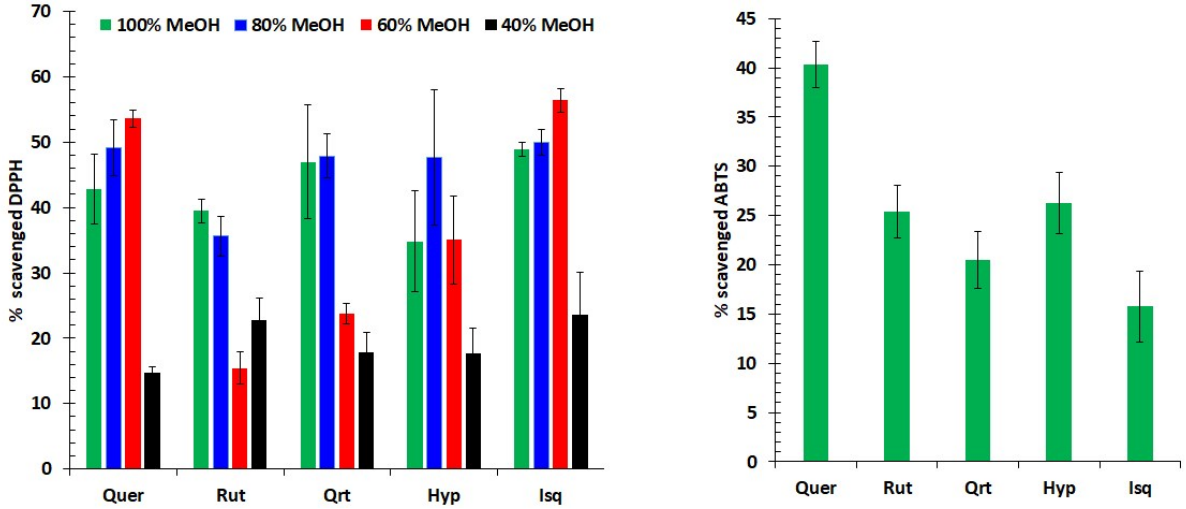

Figure S7. ***Left****-DPPH bleaching assay at different methanol concentrations.* ***Right****- ABTS bleaching assay of the studied compound.*

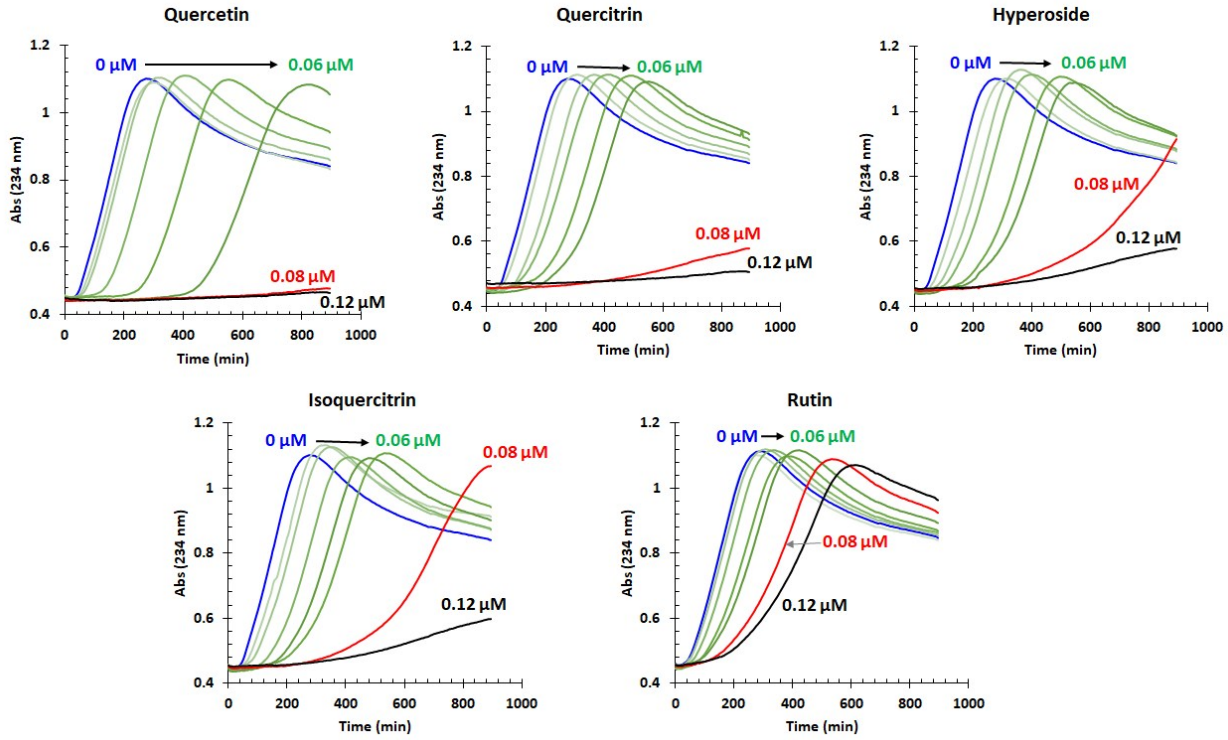

Figure S8. *Kinetic profile of liposome peroxidation, measured at 234 nm, and their inhibition by the studied glycosides in a concentration-dependent manner.*

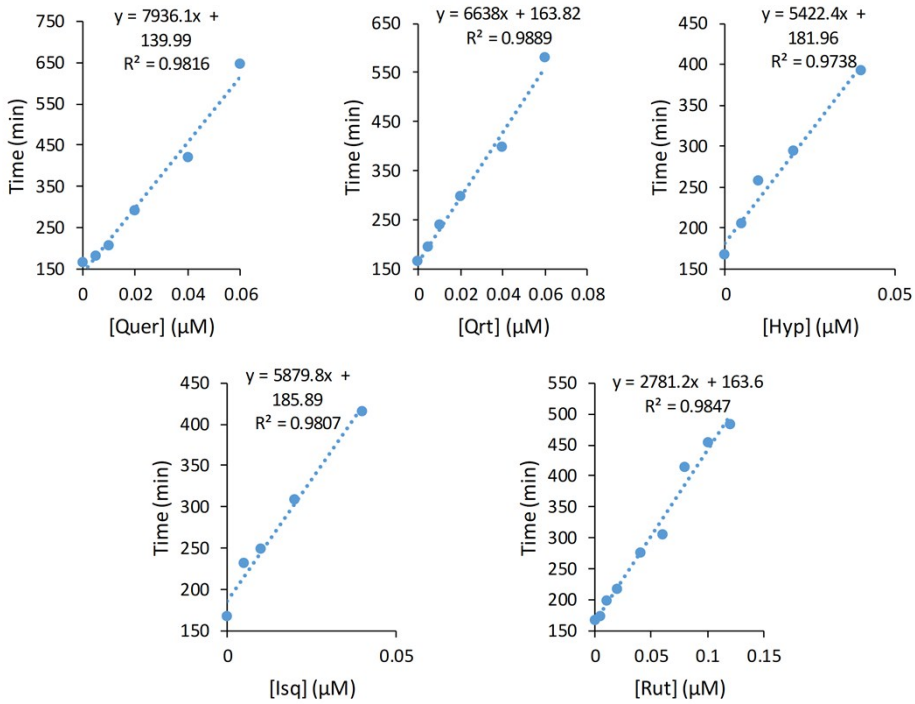

Figure S9. *Antioxidant capacity evaluation using inhibition liposomes peroxidation assay: lag time linear dependence on compounds concentration. Lag time values correspond to the inflection points in the kinetic profiles from Figure 8, main text.*

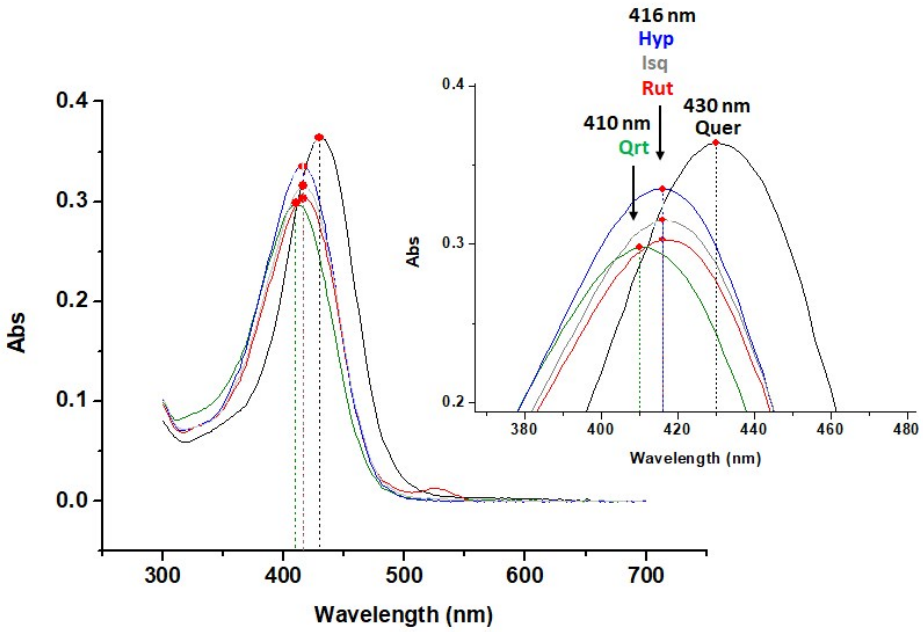

Figure S10. *Molecular absorption spectra recorded upon treatment of the investigated glycosides and quercetin with $AlCl_3$ as described in main text. Inset: Zoomed in for the spectral maxima.*