Media effects on the mechanism of antioxidant action of silybin and 2,3-dehydrosilybin: The role of enol group

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Figure S1. ^{1}H NMR spectrum of 2,3-dehydrosilybin in acetone-d_6 (200 MHz).

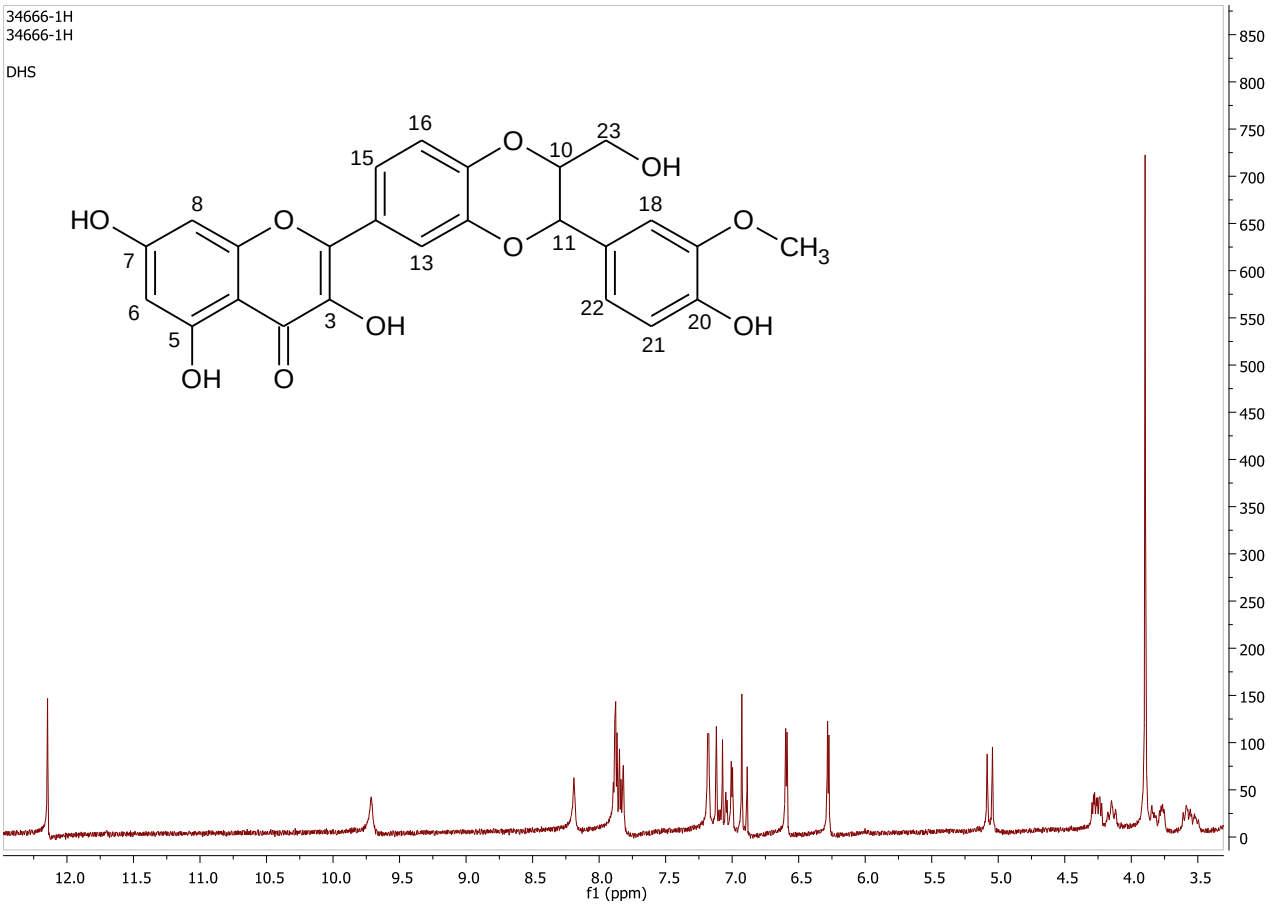


Figure S2. ^{1}H NMR spectrum of 2,3-dehydrosilybin in DMSO-d_6 (500 MHz).

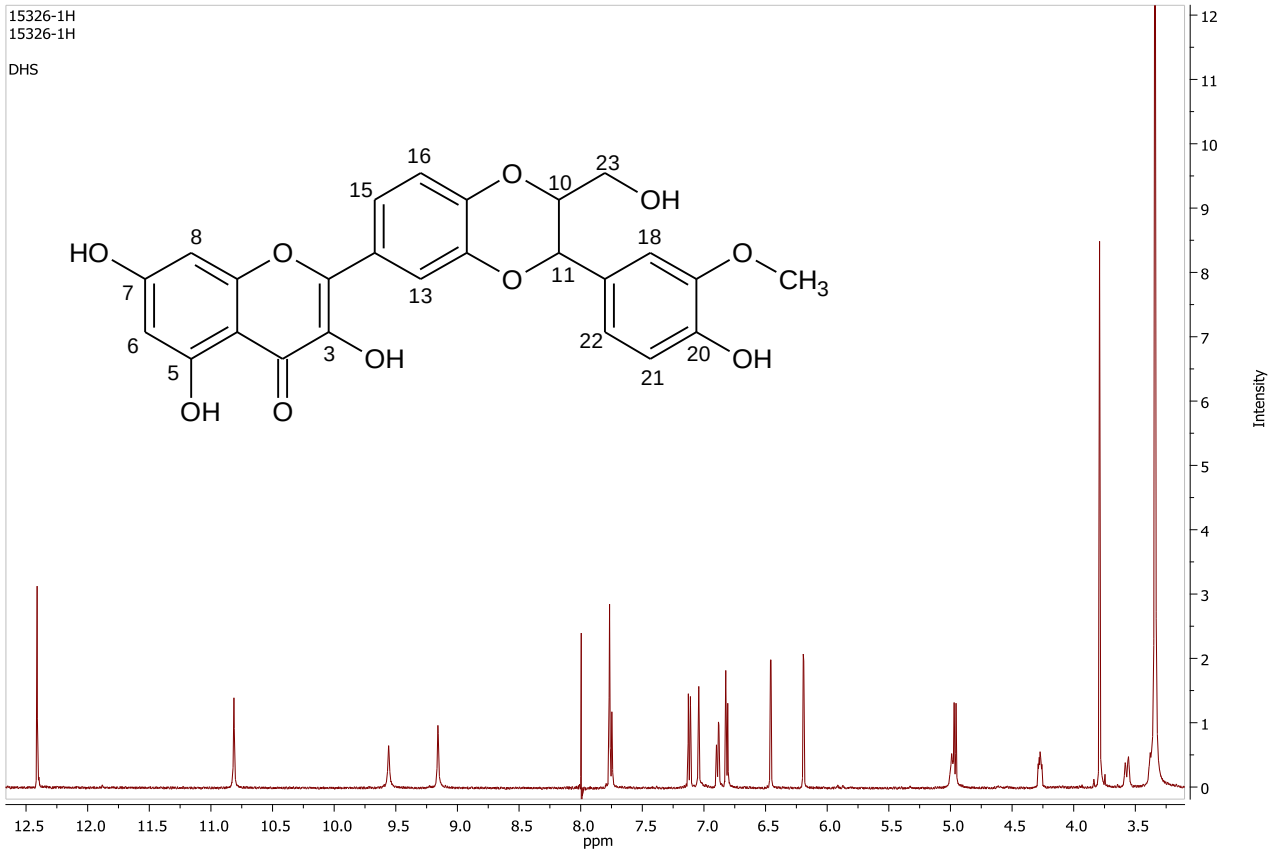
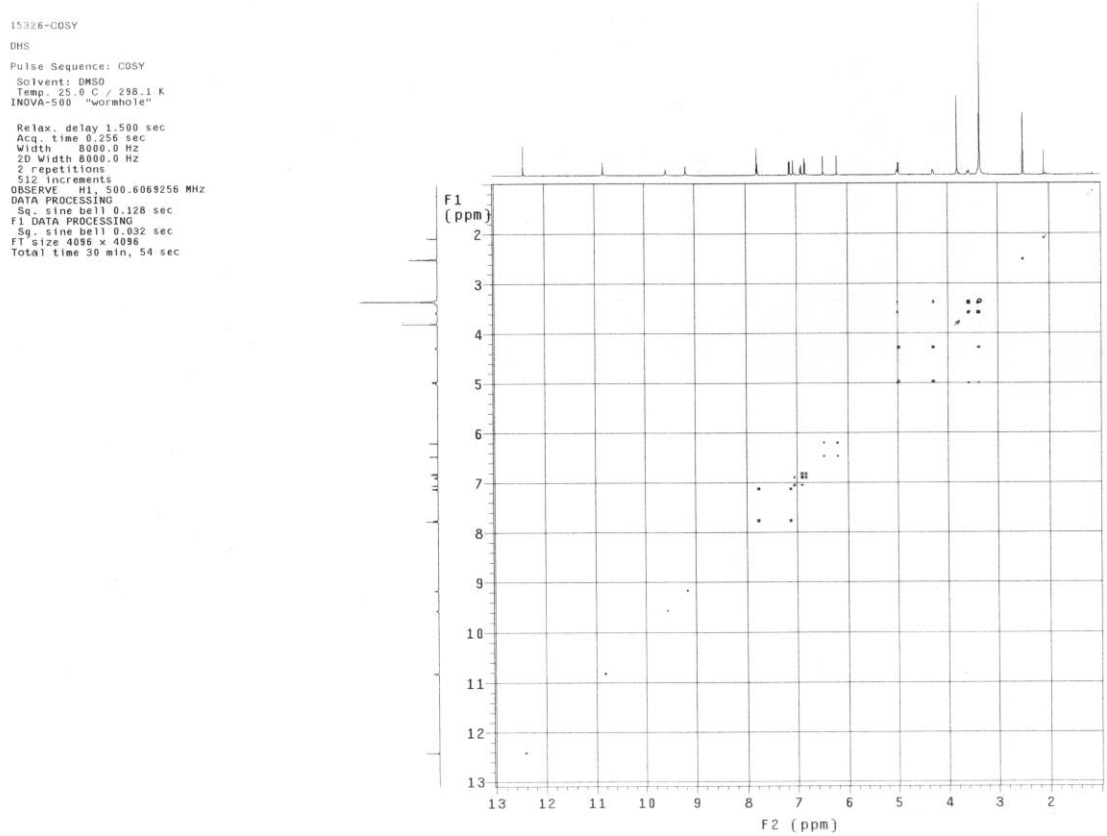


Figure S3. ^{1}H NMR COSY spectrum of 2,3-dehydrosilybin in DMSO-d_6 (500 MHz).



15326-COSY

DHS

Pulse Sequence: COSY
Solvent: DMSO
Temp. 25.0 C / 298.1 K
INOVA-500 "wormhole"

Relax. delay 1.500 sec
Acq. time 0.256 sec
Width 8000.0 Hz
2D Width 8000.0 Hz
2 repetitions
512 increments
OBSERVE H1, 500.6069256 MHz
DATA PROCESSING
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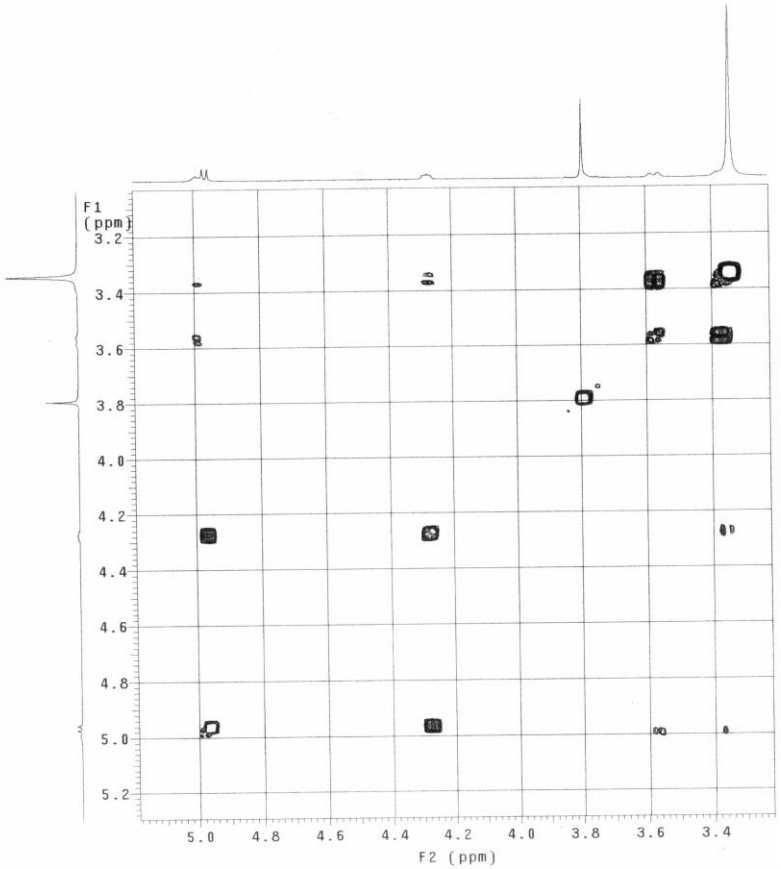
F1 DATA PROCESSING
Sq. sine bell 0.032 sec
FT size 4096 x 4096
Total time 30 min, 54 sec



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Pulse Sequence: COSY
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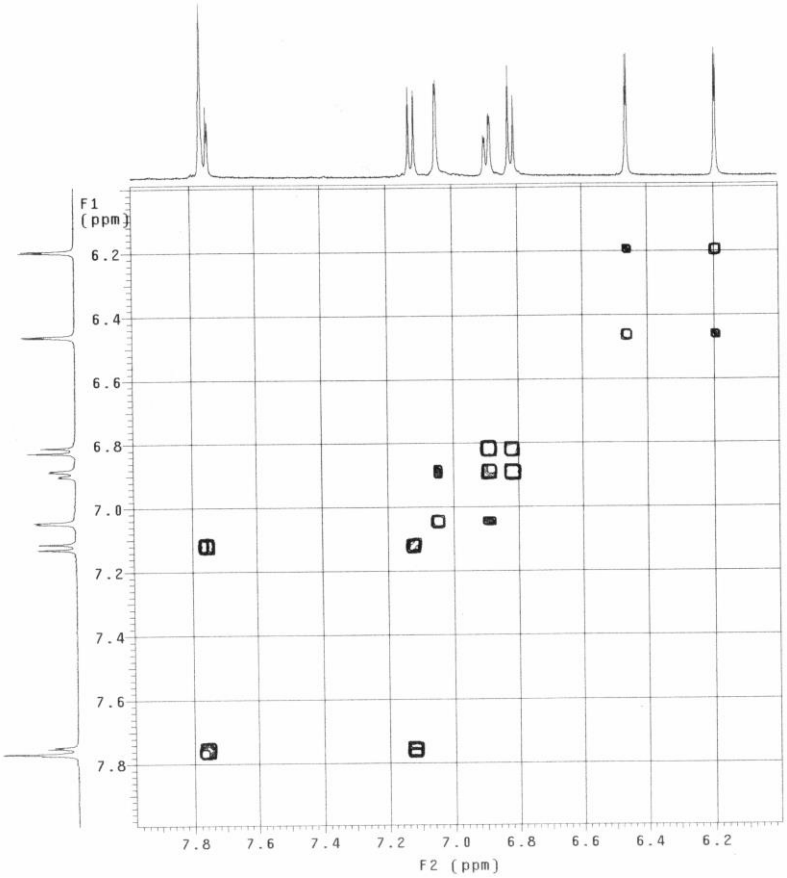


Table S1. Comparison of ^{1}H NMR data for 2,3-dehydrosilybin with literature data.

proton	Gazak et al. (ref. 26)			Our work (DMSO-d_6)		
	δ / ppm	multiplicity	J / Hz	δ / ppm	multiplicity	J / Hz
23 (1)	3.373	ddd	12.3, 5.0, 2.6	3.36	m	
23 (2)	3.573	ddd	12.3, 5.1, 4.5	3.57	m	
OMe	3.792	s		3.79	s	
10	4.275	ddd	7.9, 4.5, 2.5	4.27	m	
11	4.967	d	7.9	4.96	d	7.9
23-OH	4.967	dd	5.1, 5.0	4.99	m	
6	6.194	d	2.0	6.19	d	2.1
8	6.459	d	2.0	6.46	d	2.1
21	6.853	d	8.1	6.81	d	8.1
22	6.891	dd	8.1, 2.0	6.89	dd	8.1, 1.9
18	7.045	d	2.0	7.04	d	1.9
16	7.120	d	9.0	7.12	d	9.0
13	7.669	d	2.2	7.74	d	2.2
15	7.756	dd	9.0, 2.2	7.77	m	
20-OH	9.130	s		9.16	s	
3-OH	9.532	s		9.56	s	
7-OH	10.788	s		10.81	s	
5-OH	12.404	s		12.41	s	

Figure S4. MS-ESI spectrum of 2,3-dehydrosilybin.

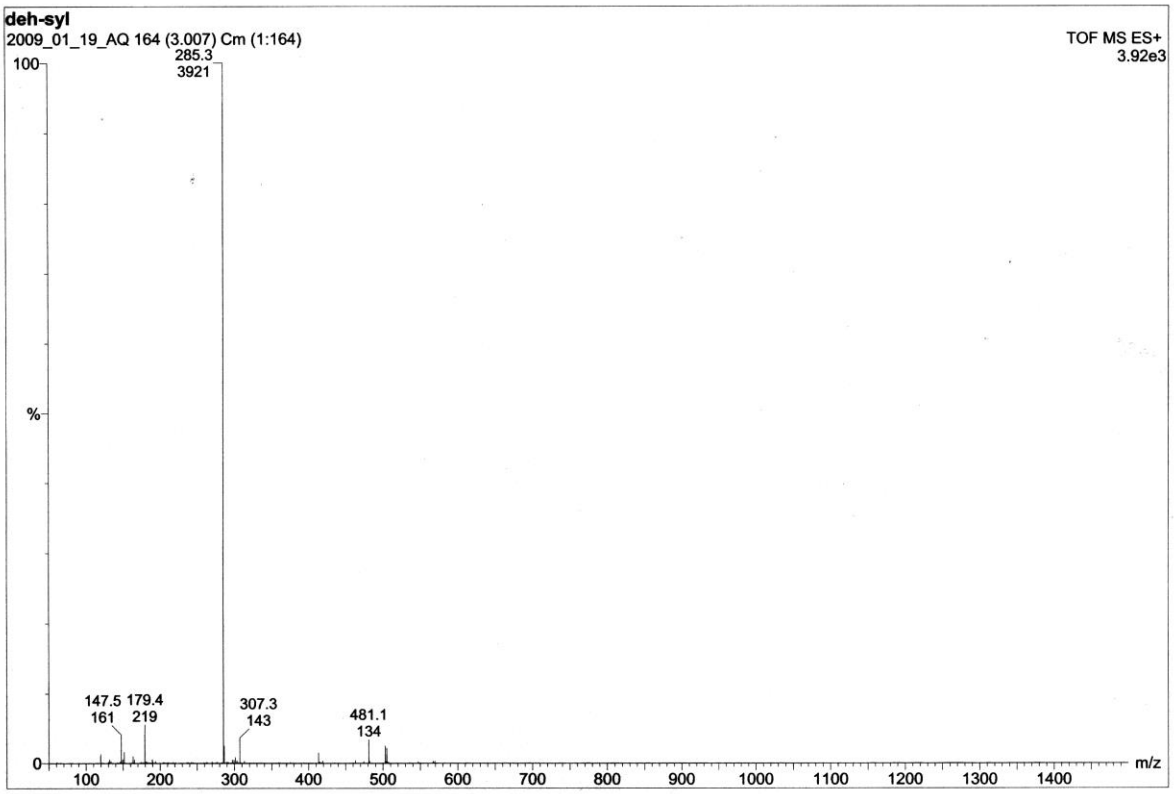


Figure S5. MS-ESI spectrum of 2,3-dehydrosilybin in the presence of sodium formate.

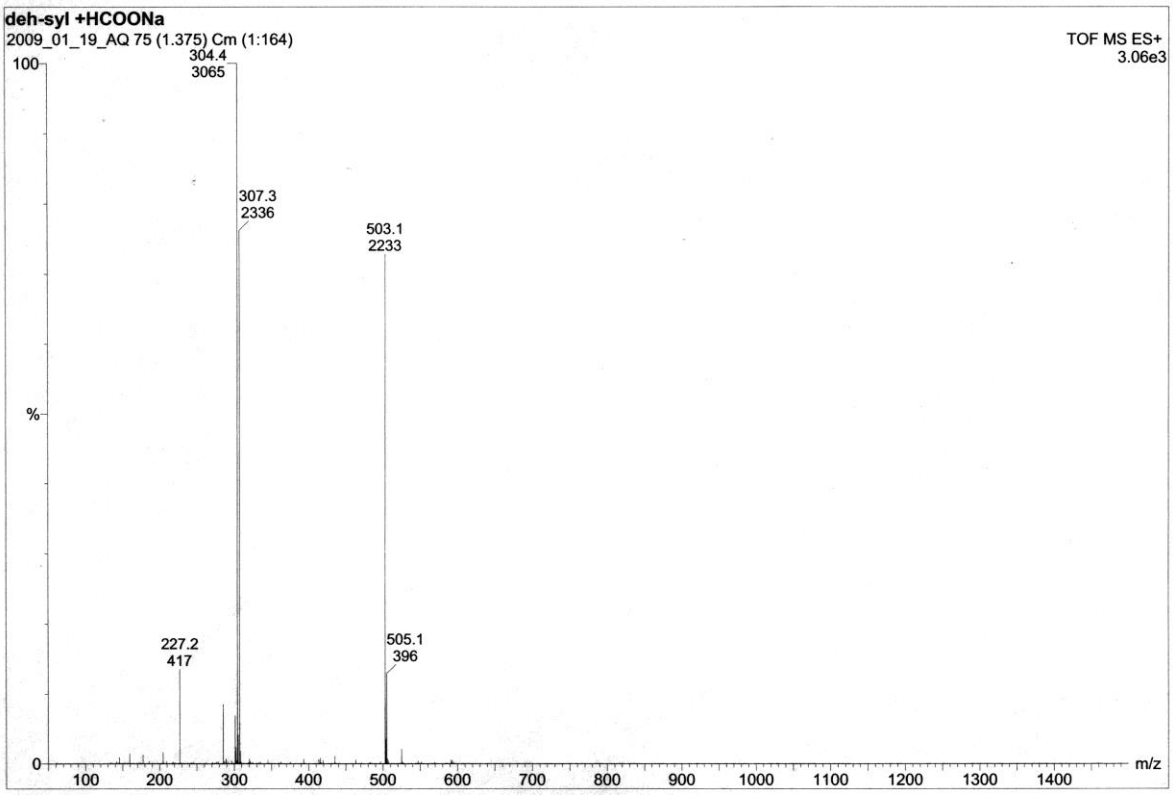


Figure S6. UV-VIS spectra of silybin (0.005 M) dissolved in phosphate buffer for 37 values of pH in the range from 1.6 to 13.5.

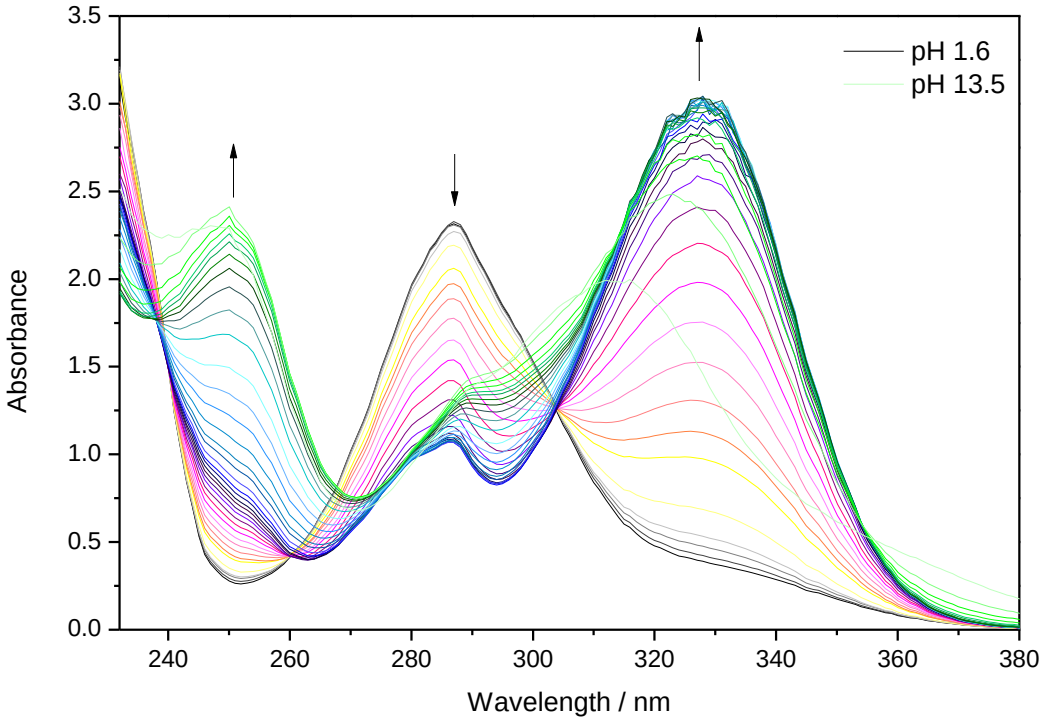


Figure S7. UV-VIS spectra of 2,3-dehydrosilybin (0.005 M) dissolved in phosphate buffer for 35 values of pH in the range from 3.2 to 13.0.

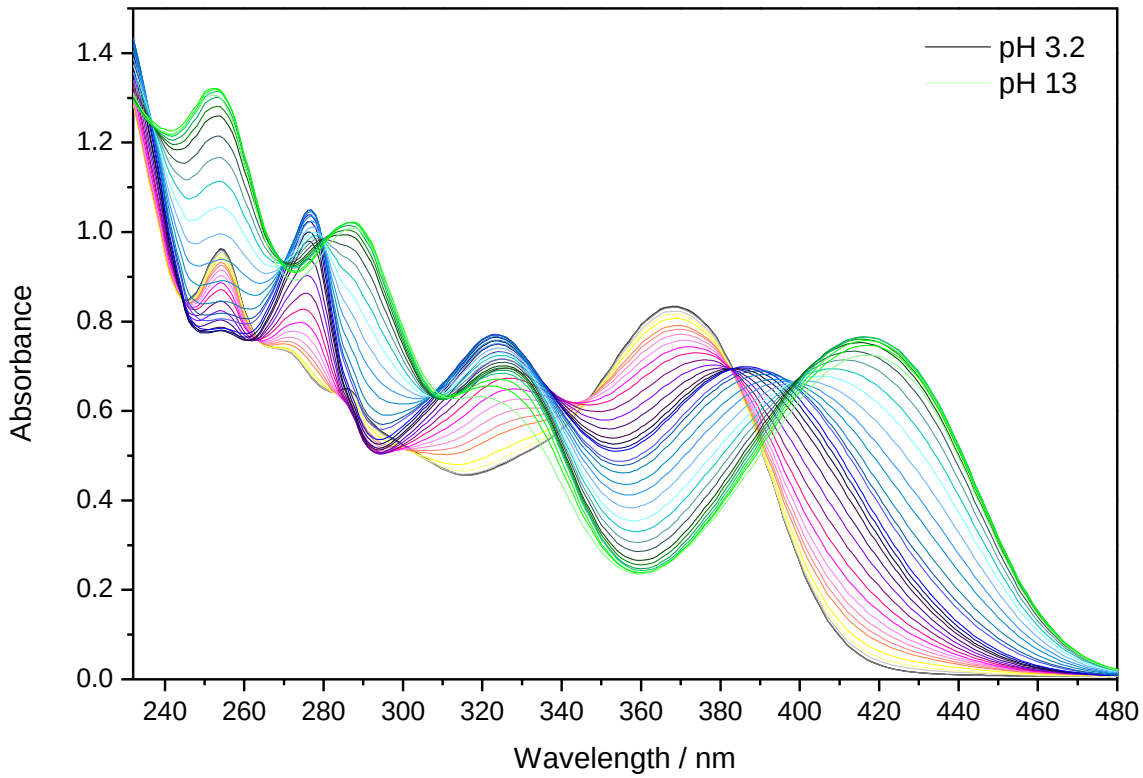


Table S2. Kinetic data for the reaction of dpph• with silybin in dioxane.

Neat dioxane	
$10^3 \times$ [ArOH]/M	$10^5 \times k_{exp}$ / s^{-1}
4.26	12.9
3.31	8.95
2.58	9.00
1.93	5.69
1.45	5.52
1.04	1.73
0.49	1.64
k = 0.030 $M^{-1}s^{-1}$	
Δ*k*[a] = 0.01 $M^{-1}s^{-1}$	
R^2=0.9418	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$\boldsymbol{k}^{\text{dioxane}}$ **= 0.03 ± 0.003 $M^{-1}s^{-1}$**

Table S3. Kinetic data for the reaction of dpph• with silybin in ethyl acetate.

Neat ethyl acetate		Neat ethyl acetate	
$10^3 \times$ [ArOH]/M	$10^4 \times k_{exp}$ / s^{-1}	$10^4 \times$ [ArOH]/M	$10^4 \times k_{exp}$ / s^{-1}
4.17	3.99	4.17	4.78
3.24	3.50	3.24	3.79
2.52	2.96	2.52	3.41
1.89	2.33	1.89	2.56
1.42	1.97	1.42	1.64
1.01	1.55	1.01	1.10
0.68	0.98	0.68	0.74
0.41	0.72	0.41	0.41
$\boldsymbol{k}$ = 0.10 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 0.12 $M^{-1}s^{-1}$	
$\Delta\boldsymbol{k}^{\mathbf{a}}$ = 0.01 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^{\mathbf{a}}$ = 0.01 $M^{-1}s^{-1}$	
R^2=0.9868		R^2=0.9816	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$\boldsymbol{k}^{\text{ethyl acetate}}$ **= 0.11 ± 0.01 $M^{-1}s^{-1}$**

Table S4. Kinetic data for the reaction of dpph• with silybin in methanol and acidified methanol.

Neat methanol		Neat methanol		methanol/ 100mM CH_3CO_2H		methanol/ 100mM CH_3CO_2H	
$10^4 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}	$10^4 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}	$10^3 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}	$10^3 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}
11.2	7.52	11.2	7.60	2.56	1.42	2.56	1.40
8.71	5.19	8.71	5.58	1.99	1.14	1.99	1.12
6.77	4.11	6.77	4.66	1.55	1.11	1.55	0.91
5.08	3.47	5.08	3.92	1.16	0.90	1.16	0.73
3.81	2.68	3.81	2.78	0.87	0.76	0.87	0.55
2.72	1.84	2.72	2.06	0.62	0.47	0.62	0.51
1.81	1.12	1.81	1.37	0.41	0.41	0.41	0.39
1.09	0.61	1.09	0.73	0.25	0.40		
$\boldsymbol{k}$ = 6.43 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 6.52 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 0.46 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 0.47 $M^{-1}s^{-1}$	
$\Delta\boldsymbol{k}^{\mathbf{a}}$ = 0.54 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^{a}$ = 0.45 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^{a}$ = 0.07 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^{a}$ = 0.03 $M^{-1}s^{-1}$	
R^2=0.9879		R^2=0.9918		R^2=0.9567		R^2=0.9958	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$\boldsymbol{k}^{\text{methanol}}$ **= 6.48 ± 0.05 $M^{-1}s^{-1}$**
$\boldsymbol{k}^{\text{methanol/100mM CH3CO2H}}$ **= 0.47 ± 0.01 $M^{-1}s^{-1}$**

Table S5. Kinetic data for the reaction of dpph• with silybin in the mixture of solvents (methanol – water 1:1, v/v, pH = 5.5).

$10^3 \times$ [ArOH]/M	$10^2 \times k_{exp}$ / s^{-1}	$10^3 \times$ [ArOH]/M	$10^2 \times k_{exp}$ / s^{-1}
1.25	2.30	1.25	2.16
0.97	1.82	0.97	1.87
0.76	1.49	0.76	1.37
0.44	0.69	0.59	0.89
0.33	0.47	0.44	0.68
0.25	0.46	0.33	0.65
0.18	0.39	0.25	0.32
		0.18	0.22
k = 19.0 $M^{-1}s^{-1}$		***k*** = 18.81 $M^{-1}s^{-1}$	
Δ*k*[a] = 1.75 $M^{-1}s^{-1}$		**Δ*k*[a]** = 1.99 $M^{-1}s^{-1}$	
R^2=0.9883		R^2=0.9810	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$\boldsymbol{k}^{\text{pH 5.5}}$ **= 18.9 ± 0.1 $M^{-1}s^{-1}$**

Table S6. Kinetic data for the reaction of dpph• with silybin in the mixture of solvents (methanol – water 1:1, v/v, pH = 7.4).

$10^3 \times$ [ArOH]/M	$10^2 \times k_{exp}$ / s^{-1}	$10^3 \times$ [ArOH]/M	$10^2 \times k_{exp}$ / s^{-1}
1.23	3.96	1.24	2.81
0.96	2.46	0.96	2.63
0.74	2.24	0.75	1.93
0.58	1.82	0.56	1.50
0.42	1.42	0.42	0.80
0.31	0.91	0.32	0.64
0.22	0.42	0.23	0.49
k = 31.18 $M^{-1}s^{-1}$		***k*** = 25.48 $M^{-1}s^{-1}$	
Δ*k*[a] = 5.41 $M^{-1}s^{-1}$		**Δ*k*[a]** = 4.45 $M^{-1}s^{-1}$	
R^2=0.9597		R^2=0.9593	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$\boldsymbol{k}^{\text{pH 7.4}}$ **= 28 ± 3 $M^{-1}s^{-1}$**

Table S7. Kinetic data for the reaction of dpph$^{\bullet}$ with dehydrosilybin in dioxane.

Neat dioxane		Neat dioxane	
$10^3 \times$ [ArOH]/M	$10^4 \times k_{exp}$ / s^{-1}	$10^3 \times$ [ArOH]/M	$10^4 \times k_{exp}$ / s^{-1}
4.20	9.37	3.27	7.29
2.54	5.96	2.54	5.91
1.91	4.17	1.91	3.90
1.43	3.91	1.43	3.29
1.02	2.28	1.02	2.74
0.68	1.42	0.68	2.18
0.41	1.51	0.41	1.62
k = 0.22 $M^{-1}s^{-1}$		***k*** = 0.20 $M^{-1}s^{-1}$	
Δk^a = 0.02 $M^{-1}s^{-1}$		Δk^a = 0.02 $M^{-1}s^{-1}$	
R^2=0.9868		R^2=0.9818	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

k^{dioxane} **= 0.21 ± 0.01 $M^{-1}s^{-1}$**

Table S8. Kinetic data for the reaction of dpph$^{\bullet}$ with dehydrosilybin in ethyl acetate.

Neat ethyl acetate		Neat ethyl acetate	
$10^4 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}	$10^4 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}
3.31	1.66	4.25	1.83
2.57	1.58	3.31	1.44
1.93	1.41	2.57	1.27
1.03	1.00	1.93	1.19
0.69	0.91	0.69	0.96
0.41	0.75	0.41	0.78
k = 3.27 $M^{-1}s^{-1}$		***k*** = 2.43 $M^{-1}s^{-1}$	
Δk^a = 0.64 $M^{-1}s^{-1}$		Δk^a = 0.46 $M^{-1}s^{-1}$	
R^2=0.9612		R^2=0.9632	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$k^{\text{ethyl acetate}}$ **= 2.85 ± 0.4 $M^{-1}s^{-1}$**

Table S9. Kinetic data for the reaction of dpph• with dehydrosilybin in methanol and acidified methanol.

Neat methanol		Neat methanol		methanol/ 100mM CH_3CO_2H		methanol/ 100mM CH_3CO_2H	
$10^4 \times$ [ArOH]/M	$10 \times k_{exp}$ / s^{-1}	$10^4 \times$ [ArOH]/M	$10 \times k_{exp}$ / s^{-1}	$10^3 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}	$10^4 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}
6.78	2.12	12.9	3.38	2.53	5.39	2.53	5.67
5.08	1.76	7.78	1.93	1.96	4.71	1.96	4.62
3.63	1.42	5.84	1.47	1.53	3.73	1.53	3.78
2.59	1.07	4.38	1.25	1.15	3.26	1.15	2.76
1.73	0.80	3.13	0.97	0.86	1.99	0.86	2.04
1.15	0.45	2.23	0.78	0.61	1.84	0.61	1.95
0.69	0.34	1.49	0.58	0.41	1.76	0.41	1.49
0.42	0.22	0.99	0.43	0.25	1.38	0.25	1.23
		0.60	0.33				
		0.36	0.24				
k = 305.02 $M^{-1}s^{-1}$		***k*** = 240.49 $M^{-1}s^{-1}$		***k*** = 1.86 $M^{-1}s^{-1}$		***k*** = 2.00 $M^{-1}s^{-1}$	
Δk^a = 33.7 $M^{-1}s^{-1}$		Δk^a = 11.5 $M^{-1}s^{-1}$		Δk^a = 0.23 $M^{-1}s^{-1}$		Δk^a = 0.14 $M^{-1}s^{-1}$	
R^2=0.9793		R^2=0.9944		R^2=0.9742		R^2=0.9911	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

k^{methanol} **= 273 ± 32 $M^{-1}s^{-1}$**
$k^{\text{methanol/100mM CH3CO2H}}$ **= 1.9 ± 0.1 $M^{-1}s^{-1}$**

Table S10. Kinetic data for the reaction of dpph• with dehydrosilybin in the mixture of solvents (methanol – water 1:1, v/v, pH = 5.5).

$10^4 \times$ [ArOH]/M	$10 \times k_{exp}$ / s^{-1}	$10^4 \times$ [ArOH]/M	$10 \times k_{exp}$ / s^{-1}
7.23	2.67	7.23	1.74
5.63	2.44	5.63	1.59
4.22	2.20	4.22	1.40
3.16	1.94	3.16	1.20
2.37	1.58	2.37	1.10
1.70	1.43	1.70	0.90
k = 227.69 $M^{-1}s^{-1}$		***k*** = 148.76 $M^{-1}s^{-1}$	
Δk^a = 45.3 $M^{-1}s^{-1}$		Δk^a = 23.8 $M^{-1}s^{-1}$	
R^2=0.9598		R^2=0.9737	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$k^{\text{pH 5.5}}$ **= 188 ± 40 $M^{-1}s^{-1}$**

Table S11. Kinetic data for the reaction of dpph• with dehydrosilybin in the mixture of solvents (methanol – water 1:1, v/v, pH = 7.4).

$10^3 \times$ [ArOH]/M	$10 \times k_{exp}$ / s^{-1}	$10^3 \times$ [ArOH]/M	$10 \times k_{exp}$ / s^{-1}
0.88	8.32	0.88	8.62
0.68	6.51	0.68	6.91
0.51	6.13	0.51	6.56
0.38	5.53	0.38	5.67
0.29	5.06	0.29	4.85
0.21	4.05	0.21	3.89
$\boldsymbol{k}$ = 561.19 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 646.28 $M^{-1}s^{-1}$	
$\Delta\boldsymbol{k}^{a}$ = 120 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^{a}$ = 124 $M^{-1}s^{-1}$	
R^2=0.9534		R^2=0.9624	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$\boldsymbol{k}^{pH\ 7.4}$ **= 604 ± 43 $M^{-1}s^{-1}$**

Table S12. Kinetic data for the reaction of dpph• with guaiacol in methanol and acidified methanol.

Neat methanol		Methanol/ 100mM CH_3CO_2H	
$10^2 \times$ [ArOH]/M	$10 \times k_{exp}$ / s^{-1}	$10^2 \times$ [ArOH]/M	$10^3 \times k_{exp}$ / s^{-1}
6.2	5.78	6.8	9.76
4.2	4.61	4.5	7.40
2.8	3.48	3.0	5.58
1.8	2.62	2.0	4.44
1.2	2.01	1.3	3.51
0.8	1.49	0.9	2.77
$\boldsymbol{k}$ = 7.80 $M^{-1}s^{-1}$		$\boldsymbol{k}$ = 0.12 $M^{-1}s^{-1}$	
$\Delta\boldsymbol{k}^{a}$ = 0.961 $M^{-1}s^{-1}$		$\Delta\boldsymbol{k}^{a}$ = 0.006 $M^{-1}s^{-1}$	
R^2=0.9842		R^2=0.9972	

[a] Calculated as the confidence interval of the slope for 90% confidence level.

$\boldsymbol{k}^{methanol}$ **= 7.80 ± 0.8 $M^{-1}s^{-1}$**
$\boldsymbol{k}^{methanol/100mM\ CH3CO2H}$ **= 0.12 ± 0.01 $M^{-1}s^{-1}$**

Table S13. Half-peak potentials ($E_{p/2}$) vs $Hg|Hg_2SO_4$ for silybin at pH range 4-10. Scan rate 5 mVs^{-1}.

pH		**4.01**	**5.04**	**5.98**	**7.05**	**8.05**	**9.04**	**9.94**	**slope / V pH^{-1}**
$E_{p/2}$ / V	E_2 **peak**	0.183	0.120	0.054	0.001	-0.051	-0.078	-0.078	-0.058
	E_3 **peak**	0.607	0.500	0.433	0.347	0.301	-	-	-0.076

Table S14. Half-peak potentials ($E_{p/2}$) vs $Hg|Hg_2SO_4$ for silybin at pH range 4-10. Scan rate 50 mVs^{-1}.

pH		4.01	5.04	5.98	7.05	8.05	9.04	9.94	slope / V pH^{-1}
$E_{p/2}$ / V	E_2 peak	0.221	0.149	0.092	0.030	0.026	-0.062	-0.071	-0.063
	E_3 peak	0.642	0.521	0.463	0.409	0.319	0.231	0.154	-0.078

Table S15. Half-peak potentials ($E_{p/2}$) vs $Hg|Hg_2SO_4$ for 2,3-dehydrosilybin at pH range 4-10. Scan rate 5 mVs^{-1}.

pH		4.03	5.04	6.05	6.99	7.98	9	9.85	slope / V pH^{-1}
	E_{1a} peak	-	-	-	-	-0.253	-0.306	-0.329	-0.041
	E_{1b} peak	-	-	-	-	-0.178	-0.224	-0.255	-0.041
$E_{p/2}$ / V	E_1 peak	0.016	-0.029	-0.103	-0.124	-	-	-	-0.059
	E_2 peak	0.179	0.141	0.071	0.023	-0.036	-0.094	-0.138	-0.056
	E_3 peak	0.563	0.502	0.429	0.390	0.273	0.208	0.119	-0.076

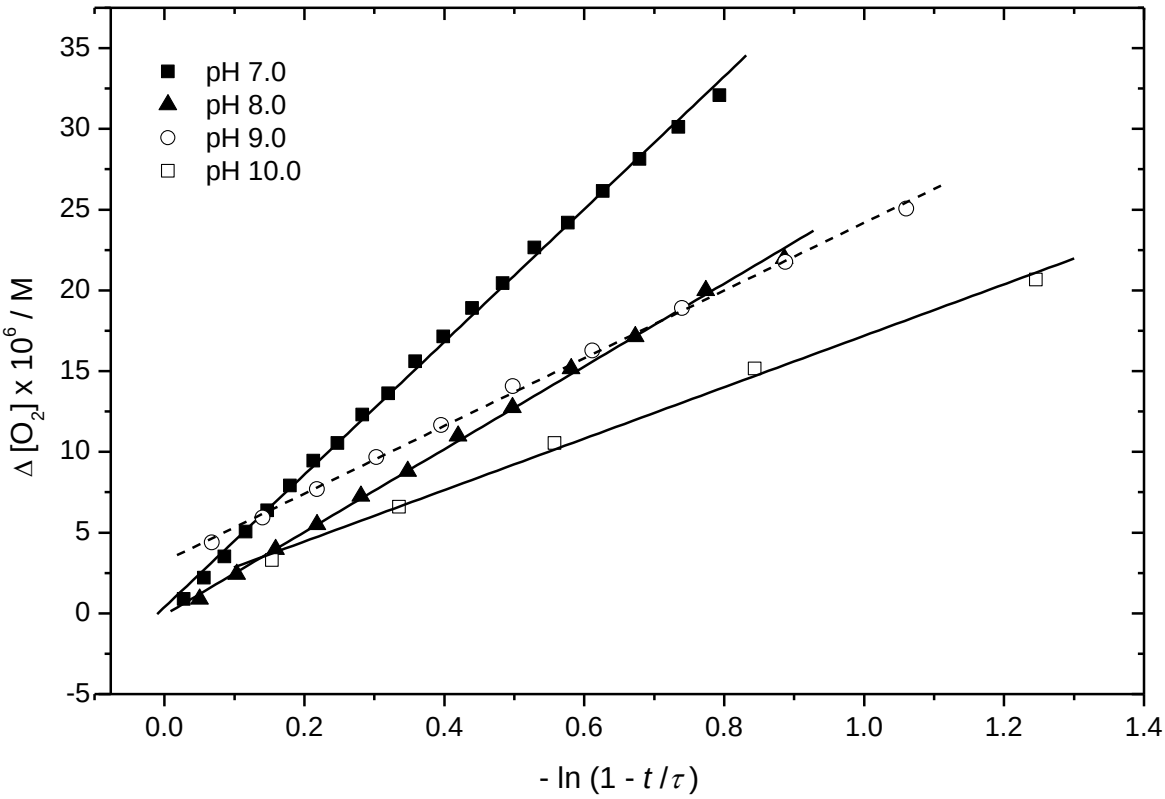
Table S16. Half-peak potentials ($E_{p/2}$) vs $Hg|Hg_2SO_4$ for 2,3-dehydrosilybin at pH range 4-10. Scan rate 50 mVs^{-1}.

pH		4.03	5.04	6.05	6.99	7.98	9	9.85	slope / V pH^{-1}
	E_1 peak	0.054	-0.004	-0.047	-0.076	-0.127	-0.196	-0.245	-0.050
$E_{p/2}$ / V	E_2 peak	0.215	0.158	0.098	0.031	-0.005	-0.077	-0.088	-0.058
	E_3 peak	0.598	0.536	0.477	0.425	0.342	0.240	0.126	-0.078

Table S17. Rates of initiation of ABAP-initiated peroxidation of 2.74 mM methyl linoleate in Triton X-100 micelles at 37°C.

pH	4.0	5.0	6.0	7.0	8.0	9.0	10.0
$10^9 \times R_i$ / Ms^{-1}	5.9	5.6	5.5	5.4	5.8	6.5	6.6

Figure S8. Plot of oxygen depletion against -ln (1 – *t* /*τ*) for 10 μM 2,3-dehydrosilybin at pH 7 – 10. The slope of each curve is equal to k_p[ML]/k_{inh}.



Calculation of O_2 molar concentration in the micellar system.

We calculated Δ [O_2], based on Δ % O_2, assuming that the solubility of oxygen in water at 37°C is 7.00 mg/dm^3 and partition coefficient of oxygen between water and micellar phase is 2.9 (Matheson, I.B.C., King Jr, A.D.J. *J. Colloid Interface Sci.* **1978**, *66*, 464). Therefore, the amount of oxygen in 1 dm^3 of organic phase is equal to 7.0 × 2.9 = 20.3 mg/dm^3. However, in 1 dm^3 of 8 mM Triton X-100 (M_w = 625 g/mol, d = 1.065 g/cm^3) the volume of organic phase is 4.69 cm^3. Thus, the total amount of oxygen dissolved is 7.0 × 0.9965 + 20.3 × 0.00469 = 7.06 mg/dm^3 = 0.221 mmol/dm^3.

Thus, 1 % O_2 = 2.2 × 10^{-3} mmol/dm^3.