Supporting Information

ESI MS studies highlight the selective interaction of Auranofin with protein free thiols⁺

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Carbonic anhydrase I	1		
Haemoglobin Superoxide dismutase Ribonuclease A	5 9 12		
		Ubiquitin	15

Carbonic anhydrase I



Figure 3 Deconvoluted ESI-Q-TOF mass spectrum of CAI solution 7×10^{-7} M incubated for 24 h with AF (3:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 4 Deconvoluted ESI-Q-TOF mass spectrum of CAI solution 7×10^{-7} M incubated for 72 h with AF (3:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 5 Deconvoluted ESI-Q-TOF mass spectrum of CAI solution 7×10^{-7} M incubated for 24 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 6 Deconvoluted ESI-Q-TOF mass spectrum of CAI solution 7×10^{-7} M incubated for 48 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 7 Deconvoluted ESI-Q-TOF mass spectrum of CAI solution 7×10^{-7} M incubated for 72 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 8 Deconvoluted ESI-Q-TOF mass spectrum of CAI solution 7×10^{-7} M incubated for 2 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 9 Deconvoluted ESI-Q-TOF mass spectrum of CAI solution 7×10^{-7} M incubated for 24 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.

Haemoglobin



Figure 10 Deconvoluted ESI-Q-TOF mass spectrum of Hb solution 10⁻⁷ M incubated for 24 h with AF (1:3 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 11 Deconvoluted ESI-Q-TOF mass spectrum of Hb solution 10^{-7} M incubated for 72 h with AF (1:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 12 Deconvoluted ESI-Q-TOF mass spectrum of Hb solution 10⁻⁷ M incubated for 24 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 13 Deconvoluted ESI-Q-TOF mass spectrum of Hb solution 10⁻⁷ M incubated for 48 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 14 Deconvoluted ESI-Q-TOF mass spectrum of Hb solution 10^{-7} M incubated for 72 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 15 Deconvoluted ESI-Q-TOF mass spectrum of Hb solution 10^{-7} M incubated for 2 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 16 Deconvoluted ESI-Q-TOF mass spectrum of Hb solution 10⁻⁷ M incubated for 24 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.

Superoxide dismutase



Figure 17 Deconvoluted ESI-Q-TOF mass spectrum of SOD solution 10⁻⁷ M incubated for 24 h with AF (3:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 18 Deconvoluted ESI-Q-TOF mass spectrum of SOD solution 10^{-7} M incubated for 24 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 19 Deconvoluted ESI-Q-TOF mass spectrum of SOD solution 10⁻⁷ M incubated for 48 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 20 Deconvoluted ESI-Q-TOF mass spectrum of SOD solution 10⁻⁷ M incubated for 72 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 22 Deconvoluted ESI-Q-TOF mass spectrum of SOD solution 10⁻⁷ M incubated for 2 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 23 Deconvoluted ESI-Q-TOF mass spectrum of SOD solution 10^{-7} M incubated for 24 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.

Ribonuclease A



Figure 24 Deconvoluted ESI-Q-TOF mass spectrum of RNaseA solution 10^{-7} M incubated for 24 h with AF (3:1 metal to protein ratio) in H_2O , pH 6.8.



Figure 25 Deconvoluted ESI-Q-TOF mass spectrum of RNaseA solution 10⁻⁷ M incubated for 24 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 26 Deconvoluted ESI-Q-TOF mass spectrum of RNaseA solution 10⁻⁷ M incubated for 48 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 27 Deconvoluted ESI-Q-TOF mass spectrum of RNaseA solution 10^{-7} M incubated for 72 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 28 Deconvoluted ESI-Q-TOF mass spectrum of RNaseA solution 10⁻⁷ M incubated for 2 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 29 Deconvoluted ESI-Q-TOF mass spectrum of RNaseA solution 10⁻⁷ M incubated for 24 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.

Ubiquitin



Figure 30 Deconvoluted ESI-Q-TOF mass spectrum of Ub solution 10^{-7} M incubated for 24 h with AF (3:1 metal to protein ratio) in H₂O, pH 6.8.



Figure 31 Deconvoluted ESI-Q-TOF mass spectrum of Ub solution 10^{-7} M incubated for 24 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 32 Deconvoluted ESI-Q-TOF mass spectrum of Ub solution 10^{-7} M incubated for 48 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 33 Deconvoluted ESI-Q-TOF mass spectrum of Ub solution 10^{-7} M incubated for 72 h with ebselen (1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 34 Deconvoluted ESI-Q-TOF mass spectrum of Ub solution 10^{-7} M incubated for 2 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.



Figure 35 Deconvoluted ESI-Q-TOF mass spectrum of Ub solution 10⁻⁷ M incubated for 24 h with ebselen and AF (1.5:1.5:1 metal to protein ratio) in 2 mM ammonium acetate solution, pH 6.8.