Supporting Information
for

The Medicinal Thiosulfinates from Garlic and Petiveria are
Not Radical-Trapping Antioxidants, but Lipophilic Analogs Are

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**Figure S1.** (A) Representative fluorescence (at 520 nm) intensity-time profiles from MeOAMVN-mediated (0.2 mM) oxidations of egg phosphatidylcholine liposomes (1 mM in PBS buffer, pH 7.4) containing 0.15 μM H$_2$B-PMHC and 4.5 μM of 9-triptycenesulfenic acid (red) and hexylated petivericin (black). (B) The data in (A) plotted according to Eq. (4) for 9-triptycenesulfenic acid (red) and hexylated petivericin (black).
Table S1. Relative rate constants for the reactions of 9-triptycenesulfenic acid (3) and hexylated petivericin (4) with MeOAMVN-derived peroxyl radicals derived from data in Figure 1C and 1D.

<table>
<thead>
<tr>
<th>[Antioxidant]</th>
<th>$k_{inh}^{H_2B-PMHC}/k_{inh}^{3}$</th>
<th>$k_{inh}^{H_2B-PMHC}/k_{inh}^{4}$</th>
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<tbody>
<tr>
<td>4.5</td>
<td>0.040</td>
<td>0.948</td>
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<tr>
<td>9.0</td>
<td>0.043</td>
<td>1.134</td>
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<tr>
<td>13.5</td>
<td>0.042</td>
<td>1.192</td>
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<tr>
<td>18</td>
<td>0.039</td>
<td>1.071</td>
</tr>
<tr>
<td>22.5</td>
<td>0.036</td>
<td>0.965</td>
</tr>
<tr>
<td>average</td>
<td>0.040±0.004</td>
<td>1.06±0.11</td>
</tr>
</tbody>
</table>

Figure S2. Hydroperoxide production in the oxidation of 1-palmitoyl-2-linoleyl-sn-glycero-3-phosphocholine liposomes (13.3 mM in phosphate-buffered saline, pH 7.4) initiated by MeOAMVN (150 µM) in the presence of 25 µM 4 only (red), 25 µM N-acetylcysteine only (green), or no additives (black).
**Figure S3.** Decomposition of 50 μM allicin 1 without MeOAMVN (A) or with 0.2 mM MeOAMVN and 0.15 μM H₂B-PMHC (C); and Decomposition of 50 μM petivericin 2 without MeOAMVN (B) or with 0.2 mM MeOAMVN and 0.15 μM H₂B-PMHC (D) in unilamellar egg phosphatidylcholine liposomes.
**Figure S4.** Decomposition of 7.5 µM petivericin 2 ([■]) in MeOAMVN-mediated (0.2 mM) oxidations of egg phosphatidylcholine liposomes (1 mM) containing 0.15 µM H₂B-PMHC and either 7.5 µM (A) or 15 µM NAC (B) in PBS buffer of pH 7.4 and formation of the corresponding mixed disulfide (●).

**Figure S5.** Decomposition of 7.5 µM hexylated petivericin 4 ([■]) in MeOAMVN-mediated (0.2 mM) oxidations of egg phosphatidylcholine liposomes (1 mM) containing 0.15 µM H₂B-PMHC and 7.5 µM (A) or 15 µM NAC (B) in PBS buffer of pH 7.4 and formation of the corresponding mixed disulfide (●).
Figure S6. Representative dose-response curves obtained from flow cytometry (1×10⁶ cells/mL; λ<sub>ex</sub> = 488 nm, λ<sub>em</sub> = 525±25 nm; 10,000 events) following induction of oxidative stress with diethylmaleate (DEM, 9 mM) in HEK293 cells grown in MEM media containing either hexylated petivericin (4, A), allicin (1, B) or petivericin (2, C) (5-200 μM) for 22 hours at 37 °C. Cells were incubated with the lipid peroxidation reporter C11-BODIPY<sup>581/591</sup> (1 μM) for 30 minutes prior to DEM treatment.
Figure S7. Representative dose-response curves obtained from papain inactivation assay in EDTA/sodium acetate buffer (pH 6.1) for hexylated petivericin (4, green; IC$_{50}$ = 1.0±0.1 µM), allicin (1, red; IC$_{50}$ = 1.2±0.2 µM) or petivericin (2, black; IC$_{50}$ = 1.1±0.1 µM). Papain activity was determined by measuring the rate of increase of absorbance at 410 nm.