

## Determination of ethylene-bis-dithiocarbamate and its metabolite ethylenethiourea in dry herbs by UHPLC-MS/MS

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### SUPPLEMENTARY MATERIAL

**Table S1** – Results of EBDC and ETU analysis of 103 dry herbs samples by UHPLC-MS/MS

| Sample code | Sample, plant part (scientific name)             | EBDC (mg kg <sup>-1</sup> ) | CS <sub>2</sub> (mg kg <sup>-1</sup> ) | ETU          |
|-------------|--|-----------------------------|--|--------------|
| 50/20       | Artichoke, leaf ( <i>Cynara scolymus</i> )       | nd                          | -                                      | nd           |
| 54/20       | Artichoke, leaf ( <i>Cynara scolymus</i> )       | 0.22                        | 0.13                                   | nd           |
| 88/20       | Artichoke, leaf ( <i>Cynara scolymus</i> )       | traces                      | traces                                 | nd           |
| 93/20       | Artichoke, leaf ( <i>Cynara scolymus</i> )       | nd                          | -                                      | nd           |
| 19/22       | Artichoke, leaf ( <i>Cynara scolymus</i> )       | nd                          | -                                      | nd           |
| 24/23       | Artichoke, leaf ( <i>Cynara scolymus</i> )       | nd                          | -                                      | not analyzed |
| 25/23       | Artichoke, leaf ( <i>Cynara scolymus</i> )       | nd                          | -                                      | not analyzed |
| 23/23       | Artichoke, leaf ( <i>Cynara scolymus</i> )       | nd                          | nd                                     | not analyzed |
| 49/20       | Black mulberry, leaf ( <i>Morus nigra</i> )      | nd                          | -                                      | nd           |
| 61/18       | Black mulberry, leaf ( <i>Morus nigra</i> )      | nd                          | -                                      | nd           |
| 11/19       | Angelica, leaf ( <i>Angelica officinalis</i> L.) | nd                          | -                                      | nd           |
| 84/20       | Angelica, leaf                                   | nd                          | -                                      | nd           |

| Sample code | Sample, plant part (scientific name)                           | EBDC (mg kg <sup>-1</sup> ) | CS <sub>2</sub> (mg kg <sup>-1</sup> ) | ETU          |
|-------------|--|-----------------------------|--|--------------|
|             | ( <i>Angelica officinalis</i> L.)                              |                             |  |              |
| 83/20       | Arnica, bark and leaf ( <i>Arnica montana</i> )                | traces                      | traces                                 | nd           |
| 91/20       | Arnica, bark and leaf ( <i>Arnica montana</i> )                | traces                      | traces                                 | nd           |
| 26/23       | Arnica, bark and leaf ( <i>Arnica montana</i> )                | traces                      | traces                                 | not analyzed |
| 74/20       | Arnica-do-mato, leaf ( <i>Solidago microglossa</i> )           | nd                          | -                                      | nd           |
| 92/20       | Assa-peixe, leaf ( <i>Vernonia polysphaera</i> )               | nd                          | -                                      | nd           |
| 51/20       | Barbatimão, bark ( <i>Stryphnodedron barbatiman</i> )          | nd                          | -                                      | nd           |
| 12/22       | Boldo, leaf ( <i>Boldus boldus</i> )                           | nd                          | -                                      | nd           |
| 57/20       | Boldo, leaf ( <i>Boldus boldus</i> )                           | nd                          | -                                      | nd           |
| 59/20       | Boldo, leaf ( <i>Boldus boldus</i> )                           | nd                          | -                                      | nd           |
| 82/20       | Boldo, leaf ( <i>Peumus boldus</i> )                           | nd                          | -                                      | nd           |
| 95/20       | Boldo e, leaf ( <i>Peumus boldus</i> )                         | nd                          | -                                      | nd           |
| 17/22       | Boldo, leaf ( <i>Boldus boldus</i> )                           | nd                          | -                                      | nd           |
| 23/22       | Boldo, leaf ( <i>Boldus boldus</i> )                           | nd                          | -                                      | nd           |
| 52/20       | Chamomile, flower ( <i>Matricaria recutita</i> )               | nd                          | -                                      | nd           |
| 64/20       | Chamomile, flower ( <i>Matricaria chamomilla</i> )             | nd                          | -                                      | nd           |
| 80/20       | Chamomile flower, leaf and bark ( <i>Matricaria recutita</i> ) | 0.06                        | 0.03                                   | nd           |
| 99/20       | Chamomile, flower and aerial parts ( <i>Matricaria</i> )       | nd                          | -                                      | nd           |

| Sample code | Sample, plant part (scientific name)                                | EBDC (mg kg <sup>-1</sup> ) | CS <sub>2</sub> (mg kg <sup>-1</sup> ) | ETU          |
|-------------|---|-----------------------------|--|--------------|
|             | <i>chamomilla</i> )   |                             |  |              |
| 17/23       | Chamomile, flower and aerial parts ( <i>Matricaria chamomilla</i> ) | 0.14                        | 0.08                                   | not analyzed |
| 18/23       | Chamomile, flower and aerial parts ( <i>Matricaria chamomilla</i> ) | nd                          | nd                                     | not analyzed |
| 20/22       | Chamomile, flower and aerial parts ( <i>Matricaria chamomilla</i> ) | nd                          | -                                      | nd           |
| 14/22       | Chamomile, flower and aerial parts ( <i>Matricaria chamomilla</i> ) | nd                          | -                                      | nd           |
| 30/23       | Chamomile, flower and aerial parts ( <i>Matricaria chamomilla</i> ) | nd                          | -                                      | not analyzed |
| 102/20      | Canela de velho, leaf ( <i>Miconia albicans</i> )                   | nd                          | -                                      | nd           |
| 78/20       | Canela de velho, leaf ( <i>Miconia albicans</i> )                   | nd                          | -                                      | nd           |
| 48/20       | Carqueja, leaf ( <i>Baccharis trimera</i> )                         | nd                          | -                                      | nd           |
| 68/20       | Cáscara sagrada, bark ( <i>Rhamnus purshiana</i> )                  | nd                          | -                                      | nd           |
| 25/22       | Cáscara sagrada, bark ( <i>Rhamnus purshiana</i> )                  | nd                          | -                                      | nd           |
| 58/18       | Horse chestnut, seed ( <i>Aesculus hippocastanum</i> )              | nd                          | -                                      | nd           |
| 104/20      | Horsetail, aerial part ( <i>Equisetum arvense</i> L)                | nd                          | -                                      | nd           |
| 60/20       | Horsetail, leaf ( <i>Equisetum</i> )                                | traces                      | traces                                 | nd           |
| 70/20       | Horsetail, leaf ( <i>Equisetum hyemale</i> )                        | nd                          | -                                      | nd           |

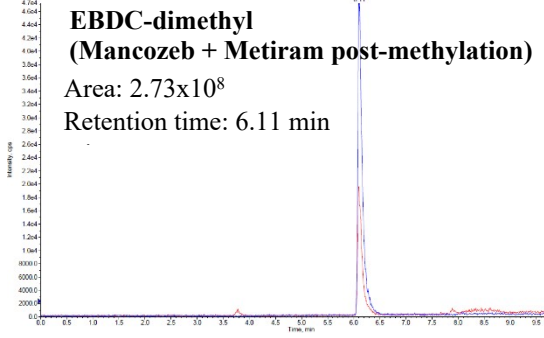
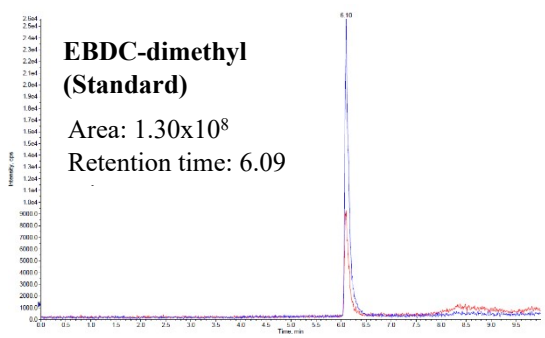
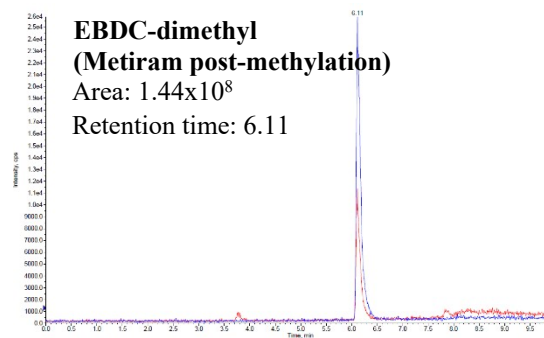
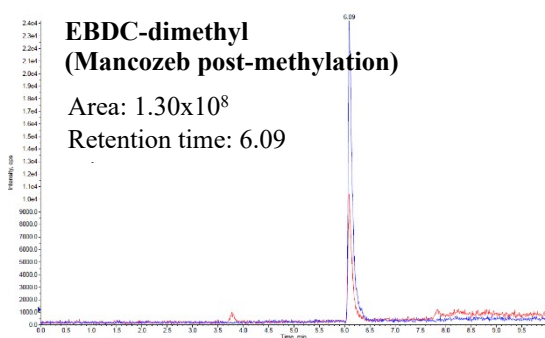
| Sample code | Sample, plant part (scientific name)  | EBDC (mg kg <sup>-1</sup> ) | CS <sub>2</sub> (mg kg <sup>-1</sup> ) | ETU          |
|-------------|---|-----------------------------|--|--------------|
| 89/20       | Horsetail, aerial part ( <i>Equitesum arvense</i> )   | 0.09                        | 0.05                                   | nd           |
| 19/23       | Horsetail, leaf ( <i>Equitesum arvense</i> )  | nd                          | -                                      | not analyzed |
| 20/23       | Horsetail, leaf ( <i>Equitesum arvense</i> )  | nd                          | -                                      | not analyzed |
| 87/20       | Gotu kola, leaf ( <i>Hydrocotyle asiatica</i> )   | 0.35                        | 0.20                                   | nd           |
| 62/18       | Gotu kola, leaf ( <i>Hydrocotyle asiatica</i> )   | nd                          | -                                      | nd           |
| 55/20       | Green tea, leaf ( <i>Camelia sinensis</i> )   | nd                          | -                                      | nd           |
| 63/20       | Green tea, leaf ( <i>Camelia sinensis</i> )   | nd                          | nd                                     | nd           |
| 90/20       | Green tea, leaf ( <i>Camelia sinensis</i> )   | traces                      | traces                                 | nd           |
| 94/20       | Green tea, leaf and stalk ( <i>Camelia sinensis</i> )   | 0.03                        | 0.02                                   | nd           |
| 22/23       | Green tea, leaf ( <i>Camelia sinensis</i> )   | nd                          | nd                                     | not analyzed |
| 27/23       | Green tea, leaf ( <i>Camelia sinensis</i> )   | traces                      | traces                                 | not analyzed |
| 29/23       | Green tea + lbitter orange, leaf + bark ( <i>Camelia sinensis</i> and <i>Citrus aurantium</i> ) | traces                      | traces                                 | not analyzed |
| 47/20       | Chapéu de couro, leaf ( <i>Echinodorus macrophyllus</i> )                                       | nd                          | -                                      | nd           |
| 85/20       | Chapéu de couro, leaf e caule ( <i>Echinodorus macrophyllus</i> )                               | nd                          | -                                      | nd           |
| 60/18       | Chapéu de couro, leaf ( <i>Echinodorus macrophyllus</i> )                                       | nd                          | -                                      | nd           |
| 98/20       | Chlorella, alga ( <i>Chlorella pyrenoidosa</i> )  | nd                          | -                                      | nd           |
| 275/18      | Chlorella, alga   | nd                          | -                                      | nd           |

| Sample code | Sample, plant part (scientific name)                  | EBDC (mg kg <sup>-1</sup> ) | CS <sub>2</sub> (mg kg <sup>-1</sup> ) | ETU          |
|-------------|---|-----------------------------|--|--------------|
|             | ( <i>Chlorella pyrenoidosa</i> )                      |                             |  |              |
| 13/19       | Comfrey, leaf ( <i>Symphytum officinale</i> )         | nd                          | -                                      | nd           |
| 56/20       | Espinheira santa, leaf ( <i>Maytenus ilicifolia</i> ) | nd                          | -                                      | nd           |
| 76/20       | Espinheira santa, leaf ( <i>Maytenus ilicifolia</i> ) | nd                          | -                                      | nd           |
| 22/22       | Espinheira santa, leaf ( <i>Maytenus ilicifolia</i> ) | nd                          | -                                      | nd           |
| 12/19       | Bladder wrack, leaf ( <i>Fucus vesiculosus</i> )      | nd                          | -                                      | nd           |
| 75/20       | Bladder wrack, leaf ( <i>Fucus vesiculosus</i> )      | nd                          | -                                      | nd           |
| 71/20       | Ginkgo, leaf ( <i>Ginkgo biloba</i> )                 | 0.07                        | 0.04                                   | nd           |
| 02/21-      | Ginkgo, leaf ( <i>Ginkgo biloba</i> )                 | 0.04                        | 0.02                                   | nd           |
| 21/23       | Ginkgo, leaf ( <i>Ginkgo biloba</i> )                 | traces                      | traces                                 | not analyzed |
| 28/23       | Ginkgo, leaf ( <i>Ginkgo biloba</i> )                 | 1.05                        | 0.59                                   | not analyzed |
| 61/20       | Guarana, seed ( <i>Paullinia cupana</i> )             | nd                          | -                                      | nd           |
| 97/20       | Guarana, seed ( <i>Paullinia cupana</i> )             | nd                          | -                                      | nd           |
| 274/18      | Guarana, seed ( <i>Paullinia cupana</i> )             | nd                          | -                                      | nd           |
| 72/20       | Hibiscus, flower ( <i>Hibiscus rosa-sinensis</i> )    | nd                          | -                                      | nd           |
| 77/20       | Hibiscus, flower ( <i>Hibiscus sabdariffa</i> )       | nd                          | -                                      | nd           |
| 58/20       | Peruvian maca, root ( <i>Lepidium meyenii</i> )       | nd                          | -                                      | nd           |
| 57/18       | Muiru puama, bark ( <i>Ptychopetalum olacoides</i> )  | nd                          | -                                      | nd           |

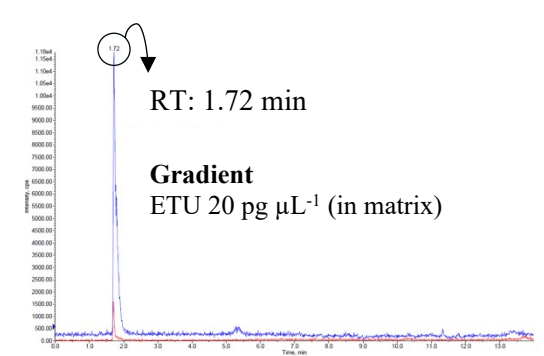
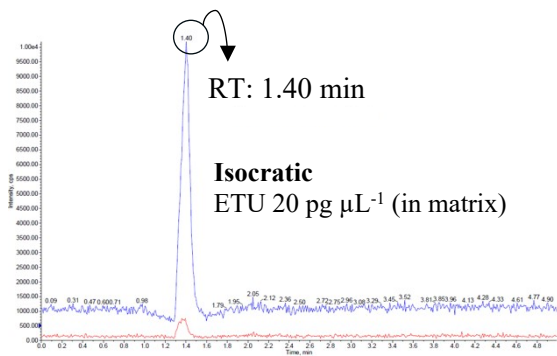
| Sample code | Sample, plant part (scientific name)                         | EBDC (mg kg <sup>-1</sup> ) | CS <sub>2</sub> (mg kg <sup>-1</sup> ) | ETU |
|-------------|--|-----------------------------|--|-----|
| 79/20       | Muirá puama, bark<br>( <i>Ptychopetalum olacoides</i> )      | nd                          | -                                      | nd  |
| 59/18       | Moringa (organic), leaf ( <i>Moringa oleifera</i> )          | nd                          | -                                      | nd  |
| 67/20       | Mulungu, bark ( <i>Erythrina velutina</i> )                  | traces                      | traces                                 | nd  |
| 106/20      | Mulungu, bark ( <i>Erythrina velutina</i> )                  | not analyzed                | -                                      | nd  |
| 100/20      | Passion fruit, leaf and stem ( <i>Passiflora incarnata</i> ) | nd                          | -                                      | nd  |
| 05/19       | Passion fruit, leaf ( <i>Passiflora alata</i> )              | nd                          | -                                      | nd  |
| 14/19       | Myrcia, leaf ( <i>Myrcia multiflora</i> )                    | nd                          | -                                      | nd  |
| 101/20      | Senna, leaf ( <i>Senna alexandrina</i> )                     | nd                          | -                                      | nd  |
| 46/20       | Senna, leaf ( <i>Cassia angustifolia</i> )                   | nd                          | -                                      | nd  |
| 62/20       | Senna, leaf ( <i>Cassia angustifolia</i> )                   | nd                          | -                                      | nd  |
| 65/20       | Senna, leaf ( <i>Cassia angustifolia</i> )                   | 0.03                        | 0.02                                   | nd  |
| 96/20       | Senna, leaf ( <i>Cassia angustifolia</i> )                   | nd                          | -                                      | nd  |
| 24/22       | Senna, leaf ( <i>Cassia angustifolia</i> )                   | nd                          | -                                      | nd  |
| 26/22       | Senna, leaf ( <i>Senna alexandrina</i> )                     | nd                          | -                                      | nd  |
| 28/22       | Senna, leaf ( <i>Cassia angustifolia</i> )                   | nd                          | -                                      | nd  |
| 21/22       | Senna, leaf ( <i>Cassia</i> )                                | nd                          | -                                      | nd  |

| Sample code | Sample, plant part (scientific name)                       | EBDC (mg kg <sup>-1</sup> ) | CS <sub>2</sub> (mg kg <sup>-1</sup> ) | ETU |
|-------------|--|-----------------------------|--|-----|
|             | <i>angustifolia</i> )                                      |                             |  |     |
| 13/22       | Senna, leaf ( <i>Senna alexandrina</i> )                   | nd                          | -                                      | nd  |
| 105/20      | Spirulina, algae ( <i>Spirulina plantesis</i> )            | nd                          | -                                      | nd  |
| 276/18      | Spirulina, algae ( <i>Spirulina plantesis</i> )            | nd                          | -                                      | nd  |
| 108/20      | Tribulus, fruit dry extract ( <i>Tribulus terrestris</i> ) | nd                          | -                                      | nd  |
| 18/22       | Cat's claw, bark ( <i>Uncaria tomentosa</i> )              | nd                          | -                                      | nd  |
| 11/22       | Cat's claw, bark ( <i>Uncaria tomentosa</i> )              | nd                          | -                                      | nd  |
| 273/18      | Cat's claw, bark ( <i>Uncaria tomentosa</i> )              | nd                          | -                                      | nd  |
| 107/20      | Cat's claw, bark ( <i>Uncaria tomentosa</i> )              | nd                          | -                                      | nd  |
| 45/20       | Cat's claw, leaf ( <i>Uncaria tomentosa</i> )              | nd                          | -                                      | nd  |
| 73/20       | Cat's claw, bark ( <i>Uncaria tomentosa</i> )              | nd                          | -                                      | nd  |

nd: not detected, <LOD (0.01 mg kg<sup>-1</sup>); traces: traces: ≥ LOD and < LOQ (0.03 mg kg<sup>-1</sup>)



**Figure S1.** ESI+ chromatograms of  $15 \text{ pg } \mu\text{L}^{-1}$  solutions of EBDC-dimethyl resulting from the methylation of mancozeb, metiram, EBDC-dimethyl analytical standard, and a mixture of mancozeb + metiram.



**Figure S2.** ESI+ chromatograms of ethylenethiourea  $20 \text{ pg } \mu\text{L}^{-1}$  in matrix (mixture of dry herbs) using isocratic elution (Mobile phase: 5% water + 5 mM ammonium formate (A) and 95% ACN (B); flow rate: 0.2 mL/min) and gradient elution (Mobile phase: water + 5 mM ammonium formate + 0.1 % formic acid (A) and MeOH + 5 mM ammonium formate + 0.1 % formic acid (B): flow rate: 0.2 mL/min; gradient from 10% B at 0–3 min, up to 100% B at 3–9 min, 100% B at 9–11 min, back to 10% B at 11–11.5 min, with a total run time of 14 minutes).