Supporting information

Figure S1 Biosynthesis of the alkaloid ergotamine (**4**) from dimethylallyl tryptophan (**3**). EasF is the closest functionally characterized homolog to the ergothioneine biosynthetic methyltransferase EgtD.

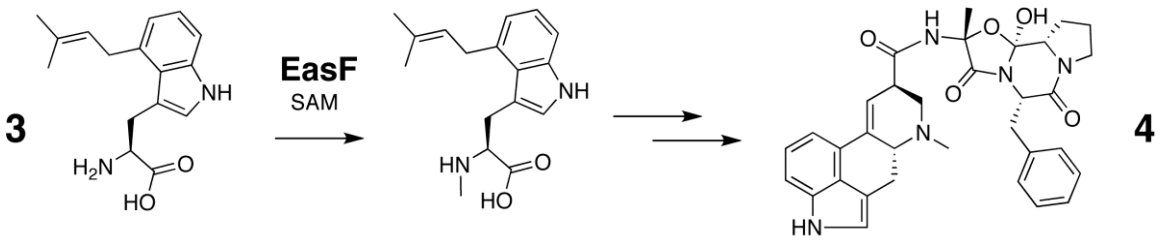

Figure S2 Analytical size-exclusion chromatography of native EgtD (blue) on an S200 10/300 GL gel filtration column (GE Healthcare). The experiment was conducted at a flow rate of 0.5 ml min^{-1} in 20 mM Tris/HCl pH 7.5, 150 mM NaCl at 283 K. A gel filtration protein standard is shown for comparison (black), where numbers correspond to the molecular weight of the proteins. EgtD elutes as a monomer of 35 kDa.

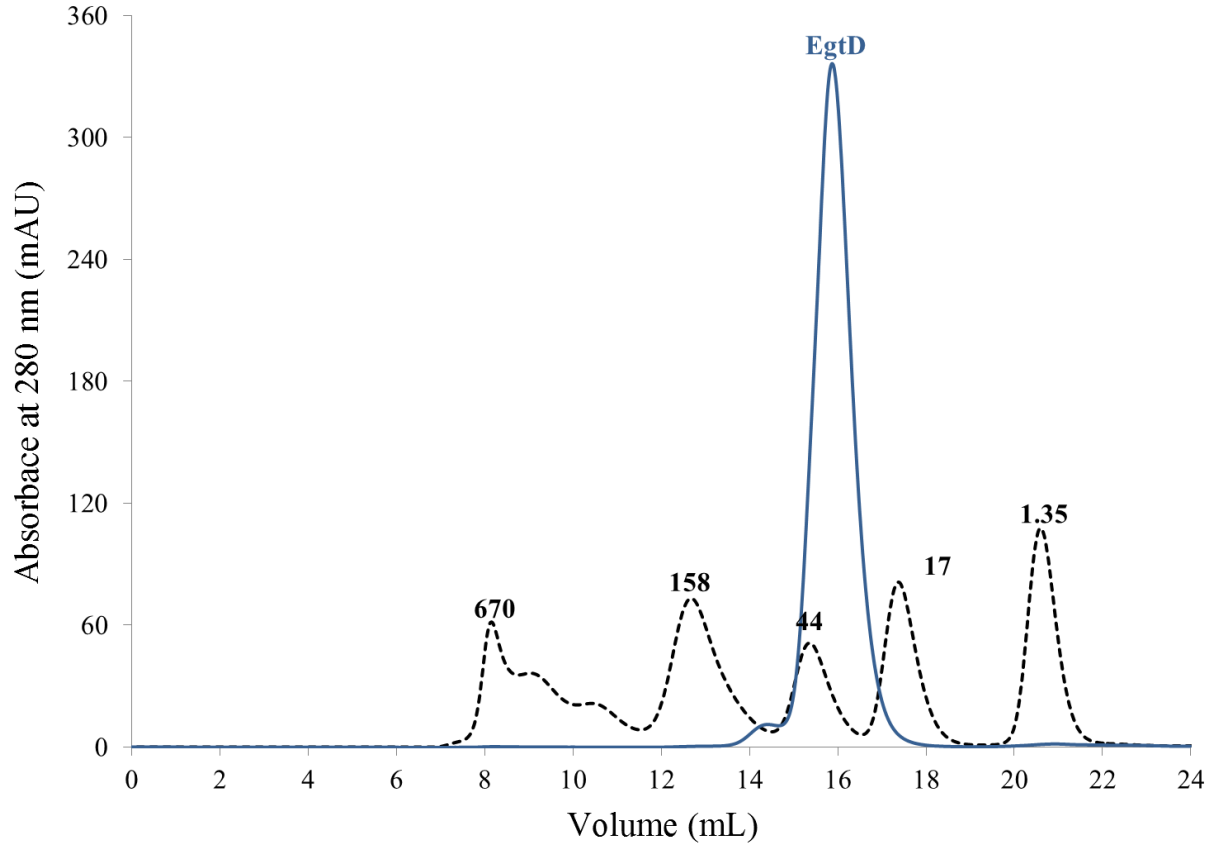

Figure S3 Excerpt from the log-file of a SHELXD Patterson search for ten anomalous scatterers in the selenium SAD data reported in Table 1. The atom numbers correspond to those shown in the Harker sections of Fig. 3.

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PSUM 52.20  PSMF Peaks: 86 78 63 62 61 60 57 54 46 42 27 23 23 22 20 20 19
Cycle 20  Peaks 99 88 85 79 76 76 69 66 66 63 14 11 8 5
R = 0.279, Min.fun. = 0.438, <cos> = 0.435, Ra = 0.299

Minimum distances (top row, 0 if special position) and PSMF (bottom row)
Peak    x      y      z      self  cross-vectors

99.9  0.5187 0.0512 0.1915   41.2                                          Atom 1
                             22.6

89.2  0.2644-0.2135 0.0803   42.6  31.2                                    Atom 2
                             17.4  39.0

85.5  0.1808-0.5460 0.0946   54.1  37.4 25.9                               Atom 3
                             33.9  41.3 28.6

79.8  0.2022-0.1280 0.1472   55.5  27.2 12.2 32.4                          Atom 4
                             35.2  31.0 23.8 16.8

77.0  0.0014-0.1749 0.2666   38.0  40.0 32.1 25.2 22.2                     Atom 5
                             48.1  24.1 28.6 26.9 16.3

76.3  0.7800 0.0559 0.1410   57.8  20.0 40.1 33.4 33.4 28.7                Atom 6
                             31.4  29.7 36.6 11.7 21.2 22.1

69.9  0.7345 0.1178 0.0324   42.1  27.4 34.4 18.8 41.5 37.2 16.1           Atom 7
                             21.0  28.9 18.3 18.8 20.9  9.7 23.8

67.0  0.1876-0.6833 0.0461   39.4  36.5 36.2 12.4 36.4 29.3 28.5 12.4      Atom 8
                             10.6  27.6 29.1 20.7 21.0 20.6 22.6 21.7

66.8  0.9370 0.0770 0.1932   41.9  30.1 35.8 32.0 25.4 20.0 13.5 26.8 32.7 Atom 9
                             11.4  40.5 18.3 19.3 15.6 20.7 14.8 15.4 15.2

63.3  0.4223 0.1059 0.1207   53.2  12.7 27.2 31.7 24.0 38.0 26.1 25.6 25.4 36.3  Atom 10
                             14.3  32.6 24.4  9.5 21.5 22.2 18.3 18.8 12.5 12.4

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14.2  0.4672-0.0597 0.0326   46.9  23.9 19.8 24.7 25.3 41.0 28.4 23.4 26.6 41.7
                              0.0  11.7  3.2  0.0  0.0  0.0  0.0  1.7  1.9  0.0

11.5  0.5235 0.1038 0.2077   39.7   4.6 35.1 36.5 30.2 38.2 20.9 28.7 36.6 29.8
                              0.0  13.0  4.7  0.5  0.0  0.6  5.5  2.4  0.0  0.0

 8.1  0.5120-0.2024 0.0019   36.6  32.5 20.9 26.0 27.9 38.4 33.5 29.3 32.4 39.5
                              0.0   5.2  1.1  8.0  0.0  4.6  2.8  0.2  2.4  6.8

 5.3  0.2686-0.3521 0.1243   52.1  30.6 12.1 16.5 17.9 30.6 33.5 29.7 27.9 29.8
                              0.0   0.0  0.0  0.0  0.0  4.1  4.5  4.1  0.1  1.6

PATFOM =  22.90

Try      2, CPU 8, CC All/Weak 52.0 / 35.9, CFOM 88.0, best 88.0, PATFOM  22.90
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