

Supplemental information

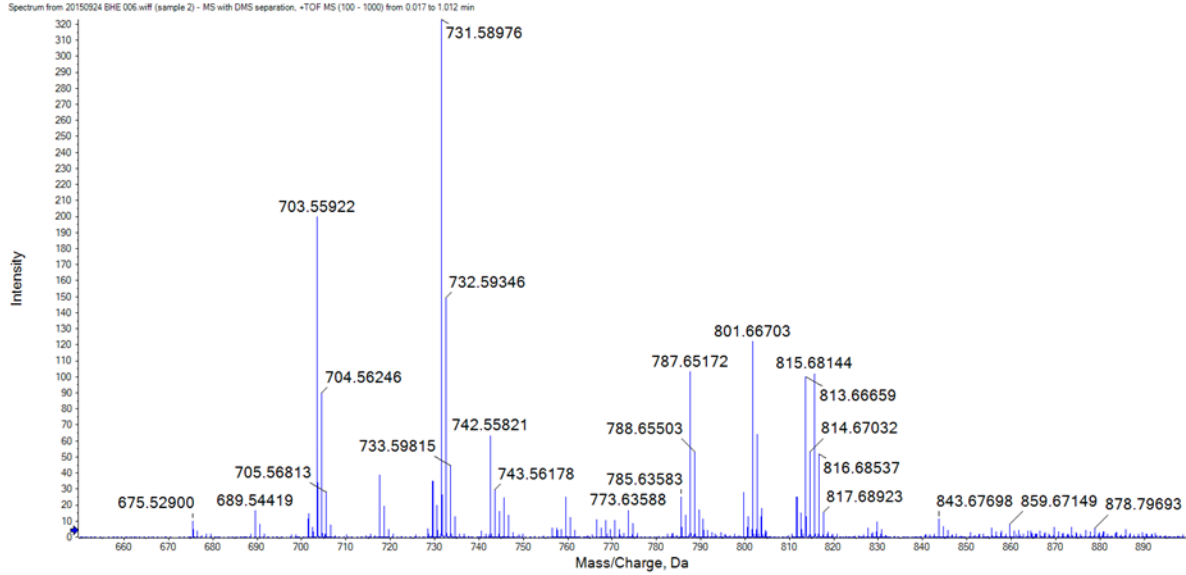
In-depth Sphingomyelin Characterization using Electron Impact Excitation of Ions from
Organics (EIEIO) and Mass Spectrometry

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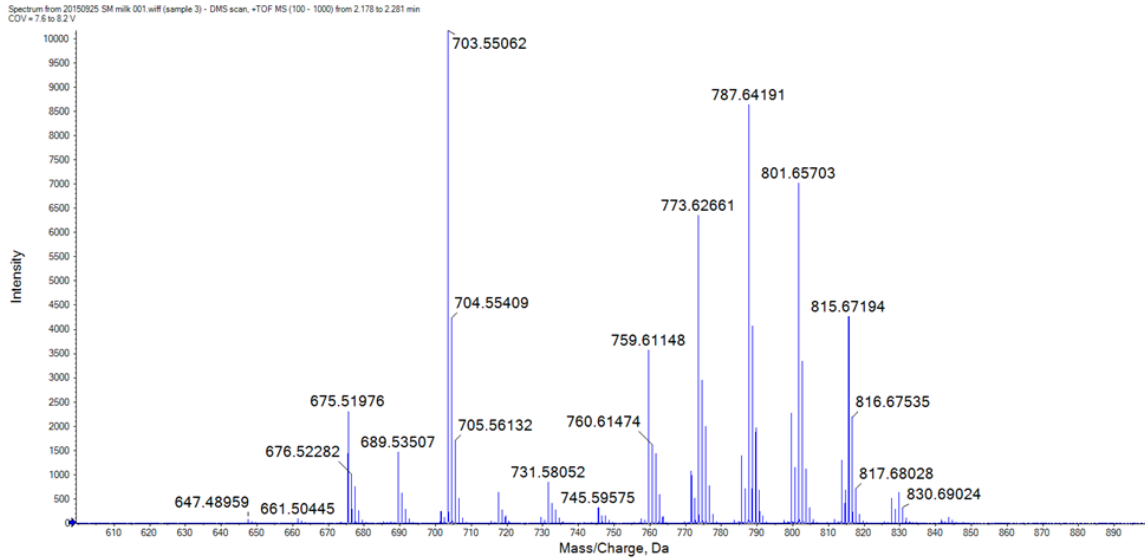
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Figure SI-1 MS spectrum and SMs found in BHE



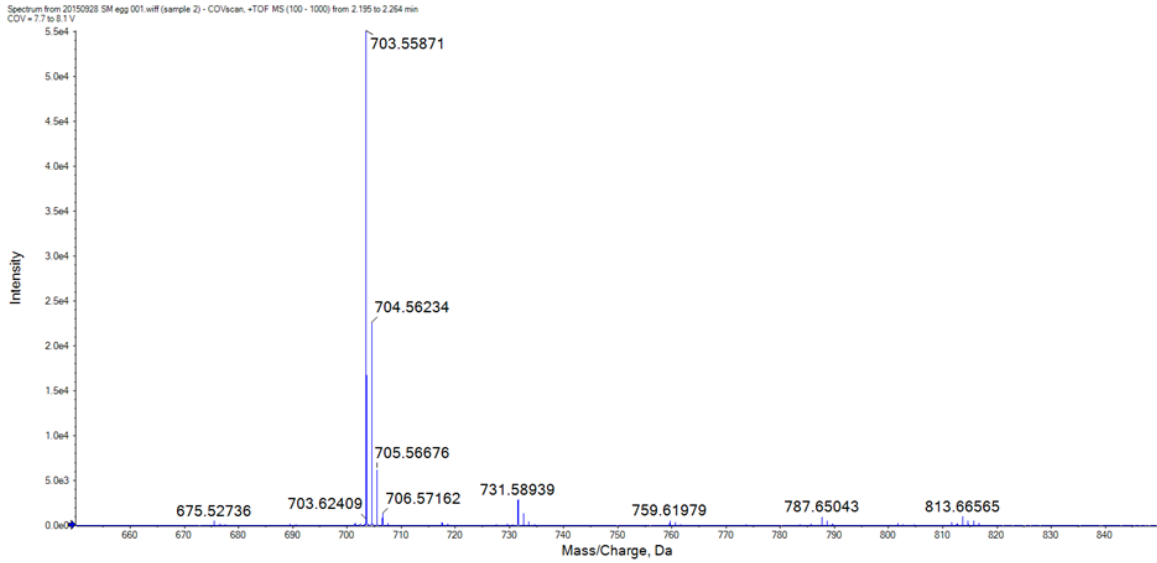
| precursor m/z | weight [%] in total | identified sphingomyelins |
|---------------|---------------------|---|
| 675.511 | 0.008 | SM(d16:1,16:0) [70%] (46 sec) |
| 689.526 | 0.017 | SM(d17:1,16:0) [100%] (14 sec) |
| 701.526 | 0.014 | SM(d18;2,16:0) [manual] |
| 703.546 | 0.186 | SM(d18:1,16:0) [95%] (0.086 sec) SM(d16:1,18:0) [5%] (5 sec) |
| 717.557 | 0.038 | SM(d17:1,18:0) [100%] (3 sec) |
| 729.555 | 0.037 | SM(d18:2,18:0) [66%] (11 sec) SM(d18:1,18:1(n-9)) [34%] (11 sec) |
| 731.572 | 0.339 | SM(d18:1,18:0) [100%] (0.032 sec) |
| 745.577 | 0.036 | SM(d19:1,18:0) [77%] (4 sec) SM(d18:1,19:0) [23%] (6 sec) |
| 759.588 | 0.034 | SM(d18:1,20:0) [88%] (4 sec) |
| 773.607 | 0.021 | SM(d17:1,22:0) [48%] (11 sec) SM(d18:1,21:0) [30%] (11 sec) SM(d16:1,23:0) [22%] (17 sec) |
| 785.609 | 0.029 | SM(d18:1,22:1) [54%] (14 sec) SM(d18:2,22:0) [46%] (14 sec) |
| 787.63 | 0.129 | SM(d18:1,22:0) [92%] (0.346 sec) SM(d17:1,23:0) [8%] (2 sec) |
| 799.624 | 0.035 | SM(d18:2,23:0) [44%] (19 sec) SM(d18:1,23:1) [30%] (19 sec) SM(d17:1,24:1) [26%] (19 sec) |
| 801.643 | 0.151 | SM(d18:1,23:0) [87%] (0.220 sec) SM(d19:1,22:0) [7%] (8 sec) SM(d17:1,24:0) [6%] (2 sec) |
| 811.623 | 0.032 | SM(d18:1,24:2(n-6,-9)) [78%] (14 sec) SM(d18:2,24:1(n-9)) [22%] (28 sec) |
| 813.644 | 0.122 | SM(d18:1,24:1(n-9)) [80%] (0.549 sec) SM(d18:2,24:0) [20%] (2 sec) |
| 815.655 | 0.139 | SM(d18:1,24:0) [91%] (0.278 sec) SM(d19:1,23:0) [9%] (5 sec) |
| 827.628 | 0.007 | PC headgroup, but may not be a SM. |
| 829.649 | 0.016 | SM(d19:1,24:0) [51%] (19 sec) SM(d18:1,25:0) [49%] (19 sec) |
| 843.636 | 0.014 | PC(17:0,16:3) + 101.11 |
| 855.605 | 0.010 | PC(17:0,16:3) + 113.05 |

Figure SI-2 MS spectrum and SMs found in milk SM



| precursor m/z | precursor intensity [%] | identified sphingomyelins |
|---------------|-------------------------|--|
| 647.486 | 0.16 | SM(d16:1,14:0) [100%] |
| 661.502 | 0.16 | SM(d17:1,14:0) [78%] SM(d16:1,15:0) [22%] |
| 673.501 | 0.04 | SM(d18:2,14:0) [52%] SM(d16:1,16:1) [48%] |
| 675.508 | 3.98 | SM(d16:1,16:0) [72%] SM(d18:1,14:0) [24%] SM(d17:1,15:0) [5%] |
| 685.511 | 0.05 | PC head group, but may not be a SM. |
| 687.517 | 0.07 | SM(d17:1,16:1) [100%] |
| 689.524 | 2.84 | SM(d17:1,16:0) [83%] SM(d18:1,15:0) [13%] |
| 699.515 | 0.02 | SM(d11:1,18:2) [100%] |
| 703.53 | 15.89 | SM(d18:1,16:0) [91%] SM(d19:1,15:0) [9%] |
| 715.544 | 0.08 | SM(d17:1,18:1) [57%] SM(d19:2,16:0) [29%] |
| 717.556 | 1.07 | SM(d19:1,16:0) [43%] SM(d18:1,17:0) [29%] SM(d17:1,18:0) [22%] SM(d20:1,15:0) [4%] SM(d16:1,19:0) [3%] |
| 727.542 | 0.02 | SM(d18:1,18:2) [100%] |
| 731.569 | 1.58 | SM(d18:1,18:0) [79%] SM(d16:1,20:0) [16%] |
| 741.581 | 0.03 | PC head group |
| 743.576 | 0.04 | SM(d19:1,18:1) [84%] |
| 745.586 | 0.59 | SM(d16:1,21:0) [55%] SM(d19:1,18:0) [23%] SM(d17:1,20:0) [14%] SM(d18:1,19:0) [8%] |
| 755.591 | 0.06 | PC_HG, but may not be a SM |
| 757.59 | 0.22 | SM(d16:1,22:1) [81%] SM(d18:1,20:1) [9%] SM(d18:2,20:0) [5%] (n-7)[84%], (n-9)[16%] |
| 759.588 | 6.84 | SM(d16:1,22:0) [88%] SM(d17:1,21:0) [7%] SM(d18:1,20:0) [4%] |
| 769.573 | 0.09 | SM(d16:1,23:2) [100%] |
| 771.596 | 2.13 | SM(d16:1,23:1) [93%] SM(d17:1,22:1) [7%] (n-6)[21%], (n-9)[79%] |
| 773.596 | 12.23 | SM(d16:1,23:0) [79%] SM(d17:1,22:0) [17%] SM(d18:1,21:0) [4%] |
| 783.608 | 0.16 | SM(d16:1,24:2(n-9,*)) [79%] SM(d18:1,22:2(n-9,*)) [13%] SM(d17:1,23:1(n-9)) |
| 785.609 | 2.73 | SM(d16:1,24:1(n-9)) [61%] [22%] SM(d18:1,22:1(n-9)) [9%] SM(d18:2,22:0) [8%] |
| 787.61 | 15.75 | SM(d18:1,22:0) [44%] SM(d16:1,24:0) [39%] SM(d17:1,23:0) [17%] |
| 789.621 | 4.09 | SM(d18:0,22:0) [manual] |
| 797.623 | 0.16 | SM(d18:2,23:1(n-9)) [56%] SM(d17:1,24:2) [19%] SM(d18:1,23:2) [14%] SM(d16:1,25:2) [11%] |
| 799.62 | 3.93 | SM(d18:1,23:1) [58%] SM(d16:1,25:1) [20%] SM(d17:1,24:1) [10%] SM(d18:2,23:0) [7%] (n-6)[6%], (n-9)[94%] |
| 801.621 | 12.64 | SM(d18:1,23:0) [77%] SM(d17:1,24:0) [12%] SM(d19:1,22:0) [12%] |
| 811.633 | 0.15 | SM(d18:1,24:2) [63%] SM(d18:2,24:1(n-9)) [32%] SM(d19:1,23:1(n-9)) |
| 813.637 | 2.47 | SM(d18:1,24:1(n-9)) [71%] [14%] SM(d18:2,24:0) [8%] SM(d17:1,25:1(n-9)) [7%] |
| 815.641 | 7.59 | SM(d18:1,24:0) [80%] SM(d19:1,23:0) [20%] |
| 825.642 | 0.07 | SM(d18:2,25:1) [39%] SM(d19:1,24:2) [21%] SM(d20:2,23:1) [19%] |
| 829.667 | 1.34 | SM(d19:1,24:0) [52%] SM(d18:1,25:0) [33%] SM(d20:1,23:0) [12%] |
| 841.674 | 0.13 | SM(d19:1,25:1(n-9)) [53%] SM(d20:2,24:0) [18%] SM(d20:1,24:1(n-9)) [16%] |
| 843.686 | 0.25 | SM(d18:1,26:0) [49%] SM(d20:1,24:0) [30%] SM(d19:1,25:0) [21%] |
| 847.657 | 0.05 | SM possible. |
| 849.622 | 0.02 | SM possible. |
| 874.726 | 0.02 | SM(d16:1,23:0)+101.11 |
| 886.698 | 0.03 | SM(d16:1,24:1)+101.11 |

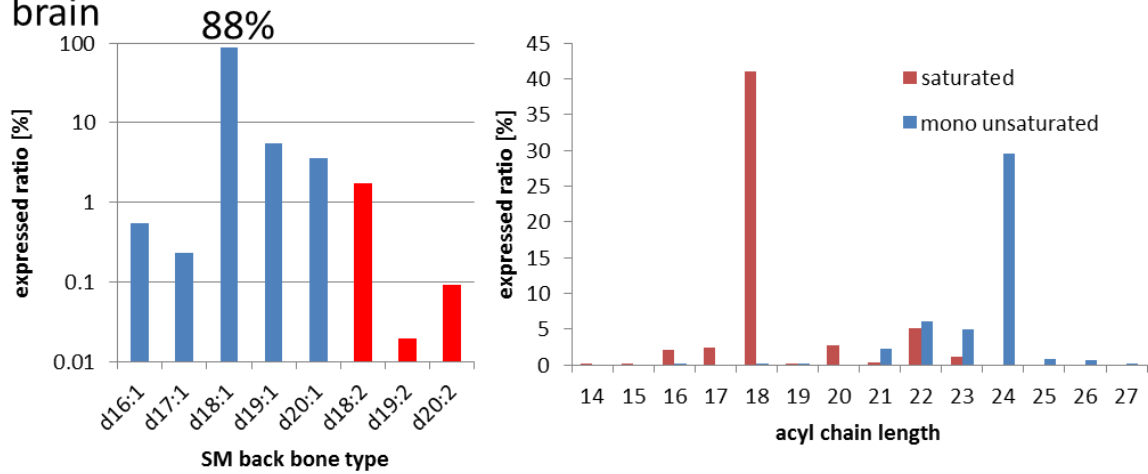
Figure SI-3 MS spectrum and SMs found in egg SM



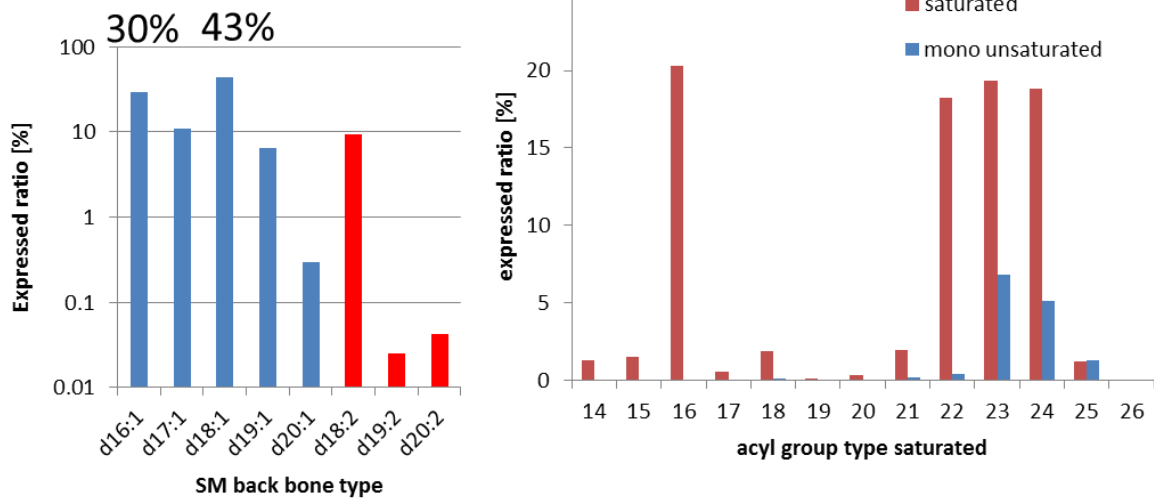
| precursor m/z | precursor intensity [%] | identified SM |
|---------------|-------------------------|---|
| 675.518 | 0.90 | SM(d18:1,14:0) [100%] |
| 685.53 | 0.03 | PC head group, but may not be a SM. |
| 689.535 | 0.34 | SM(d18:1,15:0) [55%] SM(d17:1,16:0) [41%] SM(d19:1,14:0) [5%] |
| 699.522 | 0.02 | SM(d18:1,16:2) [manual] |
| 701.534 | 0.54 | SM(d18:2,16:0) [61%] SM(d18:1,16:1(n-9)) [39%] |
| 703.518 | 83.47 | SM(d18:1,16:0) [90%] SM(d19:1,15:0) [10%] |
| 715.547 | 0.03 | SM, but chains are not identified. |
| 717.562 | 0.62 | SM(d18:1,17:0) [85%] SM(d19:1,16:0) [15%] |
| 725.531 | 0.01 | SM(d18:1,18:3) [manual] |
| 727.55 | 0.20 | SM(d18:1,18:2(n-6,-9)) [100%] |
| 729.564 | 0.41 | SM(d18:1,18:1(n-9)) [94%] SM(d18:2,18:0) [6%] |
| 731.57 | 5.36 | SM(d18:1,18:0) [94%] SM(d19:1,17:0) [6%] |
| 745.593 | 0.12 | SM(d18:1,19:0) [86%] SM(d19:1,18:0) [14%] |
| 755.579 | 0.02 | SM(d18:1,20:2) [100%] |
| 757.593 | 0.11 | SM(d18:1,20:1(n-9)) [91%] |
| 759.606 | 1.06 | SM(d18:1,20:0) [94%] SM(d19:1,19:0) [6%] |
| 773.623 | 0.14 | SM(d18:1,21:0) [100%] |
| 781.592 | 0.02 | SM(d18:1,22:3) [100%] |
| 783.607 | 0.13 | SM(d18:1,22:2(n-6,-9)) [100%] |
| 785.62 | 0.29 | SM(d18:1,22:1(n-9)) [93%] |
| 787.631 | 1.83 | SM(d18:1,22:0) [94%] |
| 799.635 | 0.07 | SM(d18:1,23:1(n-9)) [95%] |
| 801.648 | 0.44 | SM(d18:1,23:0) [92%] SM(d19:1,22:0) [8%] |
| 804.662 | 0.10 | SM(d18:1,16:0)+101.1 |
| 807.613 | 0.06 | SM(d18:1,24:4(n-6,-9,-12,-15)) [100%] |
| 809.621 | 0.12 | SM(d18:1,24:3(n-6,-9,-12)) [100%] |
| 811.633 | 0.66 | SM(d18:1,24:2(n-6,-9)) [91%] |
| 813.643 | 1.85 | SM(d18:1,24:1(n-9)) [94%] |
| 829.657 | 0.07 | SM(d18:1,25:0) [95%] |

Figure SI-4 sphingolipid backbone and acyl constituents. A: brain SM, B: milk SM, C: egg SM and D: BHE.

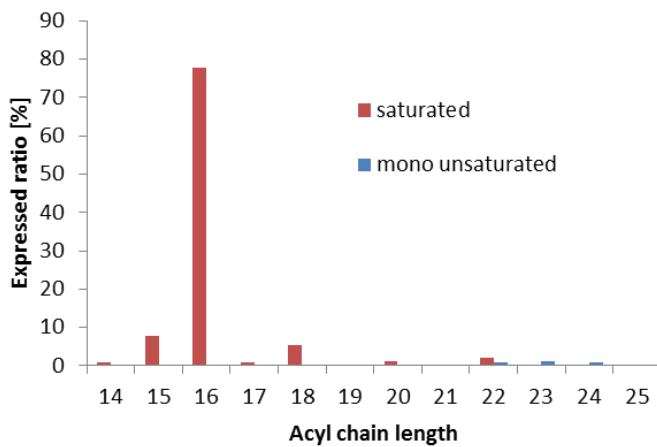
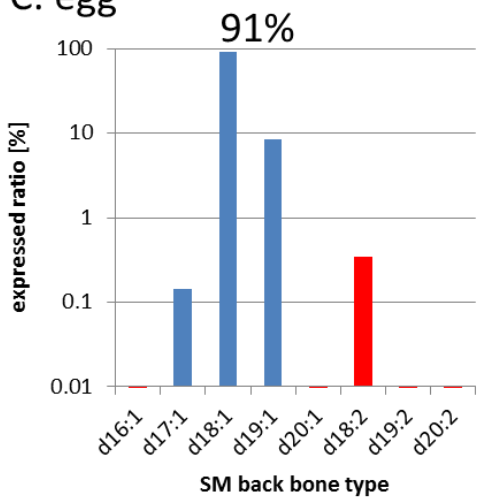
A: brain



B: milk



C: egg



D: BHE

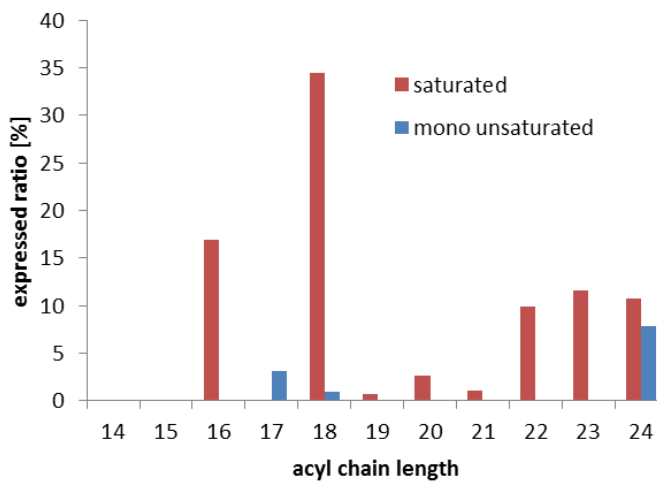
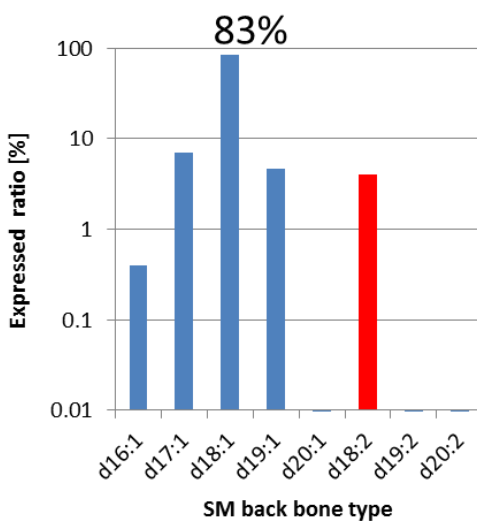


Figure SI-5 milk SM treated iodine vapor

Evaporated Milk SM was exposed to iodine vapor for 10 min. The color changed from white to deep brown. DMS separated the type of modification. (top) non modified SM profile. Hydrogen-iodine replacement reaction was observed in all types of SMs(middle). Double bond opening reaction appeared only in SM with an unsaturated allyl (bottom).

