**Electronic Supplementary Information**

**Mauveine and the mauve shade six pence stamp**

M. John Plater\* and Andrea Raab

*Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE,UK*

**LC-MS conditions**

**Separation:**

Thermo Gold C18 (150 x 2.1 mm)

Solvent A: 0.1 % v/v formic acid in water

Solvent B: 0.1 % v/v formic acid in methanol

Flow rate: 0.5 mL/min

Sample volume: 5 µL

Sample dissolved in MeOH

Gradient: 40 % A to 100 % B in 7 min

Detector A: UV 190 – 600 nm

Detector B: Maxis II positive mode, 8 Hz, auto-MSMS mode (20 eV at 200 m/z from 80 – 200 %), ES-ionisation

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| min | m/z 391 | m/z 405 | m/z 419 | m/z 433 |
| 4.5 | 1.1 |  |  |  |
| 4.7 | 21.9 | 1.1 |  |  |
| 4.9 |  | 1.3 |  |  |
| 5.0 | 7.9 | 2.6 |  |  |
| 5.1 |  | 4.1 |  |  |
| 5.3 |  | 5.0 |  |  |
| 5.4 |  |  | 1.4 |  |
| 5.5 |  | 29.1 |  |  |
| 5.6 |  |  | 1.8 |  |
| 5.7 |  |  | 15.1 |  |
| 6.0 |  |  |  | 1.7 |

Table 1: Relative peak area for authentic mauveine reported in figure 2

|  |  |  |  |
| --- | --- | --- | --- |
| min | m/z 391 | m/z 405 | m/z 419 |
| 4.6 | 2.4 |  |  |
| 4.7 | 12.7 |  |  |
| 5.0 |  | 5.8 |  |
| 5.1 | 1.7 | 17.8 |  |
| 5.3 |  | 3.8 |  |
| 5.3 |  | 2.5 |  |
| 5.4 |  | 2.2 |  |
| 5.5 |  | 17.6 |  |
| 5.6 |  |  | 3.3 |
| 5.6 |  |  | 5.4 |
| 5.8 |  |  | 21.6 |
|  |  |  |  |

**Table 2**: Relative peak area for mauveine prepared by WH Perkin’s method reported in figure 3.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | m/z 377 | m/z 391 | m/z 405 | m/z 419 | m/z 433 |
| RT (min) |  | mean (n=5) | mean (n=5) | mean (n=5) | mean (n=5) |
| 4.3 | 1.99±1.15 |  |  |  |  |
| 4.5 | 2.34±1.37 |  |  |  |  |
| 4.6 |  | 5.31±1.22 |  |  |  |
| 4.8 |  | 20.5±5.17 | 1.13±0.188 |  |  |
| 5.0 |  |  | 1.68±0.110 |  |  |
| 5.1 |  | 4.25±1.97 | 2.85±1.89 |  |  |
| 5.2 |  | 4.66±1.41 |  | 1.74±0.330 |  |
| 5.3 |  |  | 11.4±4.25 |  |  |
| 5.4 |  |  | 4.49±1.25 | 2.19±0.899 |  |
| 5.5 |  |  | 3.29±1.21 | 2.32±0.574 |  |
| 5.6 |  |  | 4.12±1.43 | 3.21±2.48 |  |
| 5.7 |  |  | 15.7±2.54 | 12.3±5.22 |  |
| 5.8 |  |  |  |  | 0.923±0.323 |
| 5.9 |  |  |  |  | 1.36±0.419 |

Table 3: relative peak area average ± SD for 5 stamps, plate 8 or 9, relative peak area above 1%, reported in figure 4 (a,d-g)

**Figure 4(a)** The extracted ion chromatogram for a six pence stamp, plate 8 or 9 is in the paper.

**Figure 4(b)** The extracted ion chromatogram for a six pence stamp, plate 6 is in the paper.

**Figure 4(c)** The extracted ion chromatogram for a six pence stamp, plate 6, Caro’s mauve, is in the paper.



Figure 4(d) Six pence stamp (2), plate 8 or 9, 1869-70 (6d), UV/VIS at 550 nm and extracted ion chromatograms



Figure 4(e) Six pence stamp (3), plate 8 or 9, 1869-70 (6d), UV/VIS at 550 nm and extracted ion chromatograms



Figure 4(f) Six pence stamp (4), plate 8 or 9, 1869-70 (6d), UV/VIS at 550 nm and extracted ion chromatograms



Figure 4(g) Six pence stamp (5), plate 8 or 9, 1869-70 (6d), UV/VIS at 550 nm and extracted ion chromatograms



Figure 4(h) Six pence stamp (2), plate 6, 1865/1867 (6d), UV/VIS at 550 nm and extracted ion chromatograms

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| min | m/z 363 | m/z 377 | m/z 391 | m/z 405 | m/z 419 | m/z 433 |
| 4.2 | 1.6 |  |  |  |  |  |
| 4.5 |  | 1.2 |  |  |  |  |
| 4.6 |  | 3.5 |  |  |  |  |
| 4.7 |  | 2.9 |  |  |  |  |
| 4.9 |  |  | 5.3 |  |  |  |
| 5.1 |  |  | 38.8 | 1.4 |  |  |
| 5.2 |  |  |  | 2.7 |  |  |
| 5.4 |  |  | 5.8 | 10.2 | 1.4 |  |
| 5.6 |  |  |  | 5.0 | 1.3 |  |
| 5.8 |  |  |  | 9.2 | 1.6 |  |
| 6.0 |  |  |  |  | 4.3 |  |
| 6.1 |  |  |  |  |  | 2.1 |

Table 4: relative peak area average ± SD for plate 6, stamp (1) reported in Figure 4b in the paper.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| min | m/z 363 | m/z 377 | m/z 391 | m/z 405 | m/z 419 | m/z 433 |
| 4.2 | 1.4 |  |  |  |  |  |
| 4.6 |  | 3.0 |  |  |  |  |
| 4.7 |  | 6.4 |  |  |  |  |
| 4.8 |  |  | 3.6 |  |  |  |
| 5.0 |  |  | 38.2 |  |  |  |
| 5.1 |  |  |  | 1.2 |  |  |
| 5.4 |  |  | 7.4 |  |  |  |
| 5.6 |  |  |  | 13.9 | 1.2 |  |
| 5.8 |  |  |  | 4.1 | 1.4 |  |
| 6.0 |  |  |  | 9.2 | 4.6 |  |

Table 5: relative peak area average ± SD for plate 6, stamp (2) for Figure 4h above, extracted ion chromatogram.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| min | m/z 363 | m/z 377 | m/z 391 | m/z 405 | m/z 419 |
| 4.2 | 19.2 |  |  |  |  |
| 4.5 |  | 2.5 |  |  |  |
| 4.6 |  | 22.2 |  |  |  |
| 4.8 |  | 6.5 | 1.7 |  |  |
| 5.0 |  | 4.9 | 2.3 |  |  |
| 5.1 |  |  | 12.7 |  |  |
| 5.4 |  |  | 11.9 | 2.7 |  |
| 5.5 |  |  | 3.2 | 1.4 |  |
| 5.7 |  |  |  | 2.3 |  |
| 5.8 |  |  |  | 2.9 |  |
| 6.1 |  |  |  |  | 2.1 |

Table 6: Relative peak area for a Caro mauveine stamp, plate 6, reported in Figure 4c in the paper.