Synthetic derivatives of mauveine

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Oxidation of phenosafranin and an excess of aniline gave a novel hydroxylated derivative of pseudo-mauveine. *N*-Methyl-*p*-toluidine and bis(4-methylphenyl)amine are efficient building blocks for making mauveine-related chromophores. Their oxidation with $K_2Cr_2O_7$ is believed to form nitrogen centred radicals which then couple with an aromatic amine by homolytic aromatic substitution of hydrogen. The *N*-methyl substituent and the *p*-methyl substituents are essential for the reaction to proceed. *N*-Methyl substituted chromophores were not demethylated in the reaction or by oxidation with $K_2Cr_2O_7$ in dilute H_2SO_4. *N*-Nitroso-bis(4-methylphenyl)amine rearranges smoothly to the orange compound, (2-nitro-4-methylphenyl)-4-methylphenylamine, when a solution in CH_2Cl_2 is treated with montmorillonite at room temperature for 24 h. 2,4-Dimethylaniline has been used to make a mauveine homologue. The colour of silk dyed with mauveine chromophores has been compared to the colour of silk dyed with authentic 1862 mauveine.

Keywords: mauveine, mauve, *N*-methyl-*p*-toluidine, *N*-phenyl-*p*-phenylenediamine, montmorillonite, Perkin

In 1856, Perkin filed a patent on a method for making mauveine by the oxidation of aniline sulfate with potassium dichromate in hot water.[1] This gave a black precipitate from which some mauveine was extracted with hot ethanol. The coloured product was dissolved in hot water and used to dye materials a purple colour. This invention was exploited by Perkin who set up a factory for mauveine manufacture with his father and brother in the years 1857–73 at Greenford Green and began the coal-tar dye industry.[2] Research on the molecular structure of mauveine was begun by Perkin himself[3–6] and later pursued by others[7–10] who showed that a phenazine moiety is the basic structure of mauveine. The two major components of Perkin's mauveine have been identified by NMR spectroscopy as mauveine A and mauveine B.[11,12] It is now known that over 12 homologues are present in mauveine.[13,14] The synthesis of mauveine by Perkin's method is low yielding and others have had difficulty repeating it.[15] Mechanistic studies suggest that *N*-phenyl-*p*-phenylenediamine derivatives are intermediates in mauveine synthesis.[16,17] We have shown that this cheap anti-oxidant from the rubber industry can be used for making mauveine chromophores.[16,17] We now report our studies on new synthetic routes to derivatives of mauveine chromophores and the chemistry of some novel building blocks. Mauveine is not commercially available like some early dyes such as fuchsine[18,19] and the lack of synthetic methods may have restricted its exploitation.

Results and discussion

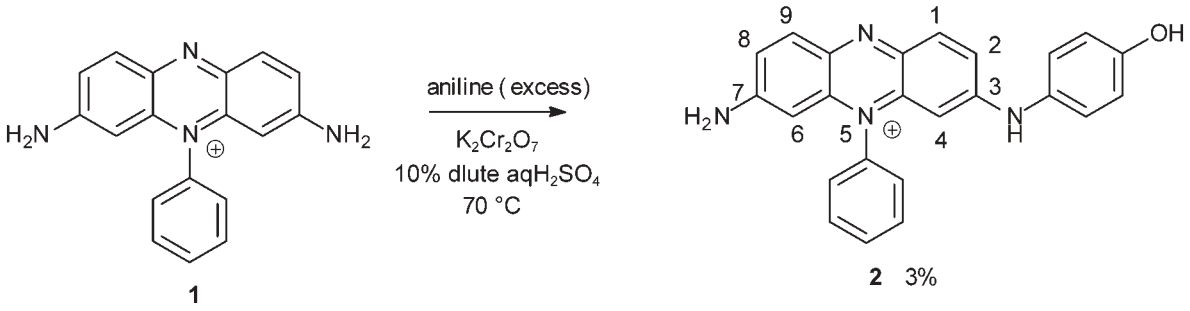
*Synthesis with phenosafranin (**1**)*

Phenosafranin **1** and a large excess of aniline were oxidised with $K_2Cr_2O_7$ in 10% dilute aq. H_2SO_4 (Scheme 1). A purple chromophore **2** was isolated in low yield. The UV showed a characteristic mauveine absorption at 551 nm[17] and the IR showed a broad absorption 2500–3300 cm^{-1}. The ^1H NMR spectrum showed two downfield doublets at 7.90 and 7.96 (2H, 1 and 9), a multiplet at 7.71–7.81 (3H, *m*/*p*-phenyl), a doublet at 7.47 (2H, *o*-phenyl) ppm, two doublets at 7.35 (1H, 2 or 8) and 7.23 (1H, 2 or 8) ppm, two doublets at 6.96 (2H, aryl) and 6.70 (2H, aryl) ppm and two fine doublets at 6.12 (1H, 4 or 6) and 5.99 (1H, 4 or 6) ppm. These data are very characteristic of a mauveine chromophore.[11,13,14] The peaks at 6.9 and 6.7 ppm are coupled doublets (J = 9.0 Hz) and are moved upfield suggesting an electron rich *para*-substituted benzene ring. High resolution mass spectrometry confirmed the molecular ion.

This reaction is best with a large excess of aniline and requires a low pH. The acid will activate the oxidant and facilitate the hydrolysis of intermediate imminium salts. Scheme 2 shows a possible route firstly involving a coupling of phenosafranin **1** and aniline to give compound **3** followed by oxidation to quinone-imine **4** via two intermediates. This would have to be reduced to product **2** with $K_2Cr_2O_7$ initially present and under the acidic conditions. Compound **4** may be a good oxidant and the excess of aniline will give a polyaniline precipitate that might act as a reductant. Presumably the build-up of product **2** is sensitive to the concentration of $K_2Cr_2O_7$ in solution and may occur once the dichromate has been consumed. Neither aniline or 4-hydroxyaniline react with phenosafranin **1** in hot water with or without acid present.

Synthesis with bis(4-methylphenyl)amine (**5**)

Since the four main components of mauveine (A, B, B_2, C)[13] contain a key building block derived from *p*-toluidine (at



Scheme 1 The synthesis of *p*-hydroxypseudo-mauveine **2**. The numbering scheme of the phenazine ring is shown.

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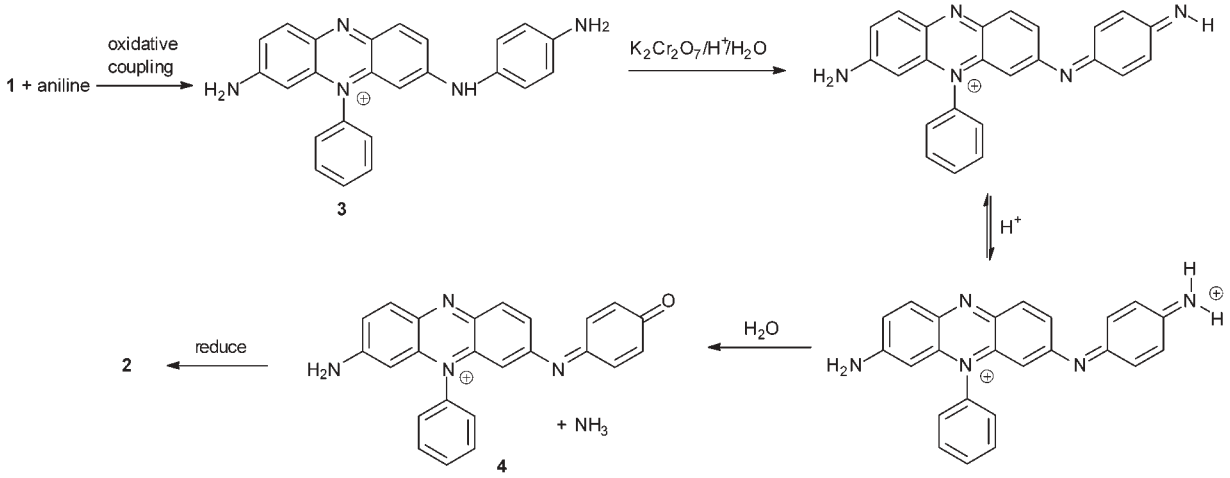


Scheme 2 A possible pathway showing four proposed intermediates leading to compound **2**.

position 3), we decided to study the dichromate oxidation of bis(4-methylphenyl)amine **5** and aniline (Scheme 3). Heating bis(4-methylphenyl)amine **5** and aniline (3 equiv.) in dilute sulfuric acid (about 0. 3 mL in 200 mL water) with $K_2Cr_2O_7$ gave a deep purple solution from which the product was isolated. Since bis(4-methylphenyl)amine **5** is poorly soluble in water so acetone was added to solubilise it. This reaction failed completely using diphenylamine, which showed that the *p*-methyl groups are essential for the reaction. The reaction presumably proceeds by formation of a nitrogen centred diaryl free radical **7** (Fig. 1) which couples to aniline by oxidative homolytic substitution of hydrogen. The next stages leading to mauveine chromophores have been discussed previously.[16,17]

The UV spectrum showed an absorption maximum at 560 nm which is shifted 10 nm bathochromically from a typical mauveine absorption maximum of 550 nm. The ^{13}C NMR spectrum showed the expected 20 aromatic resonances. The ^{1}H NMR was well resolved and included a pair of coupled doublets (8H, aryl ring) at 7.06 and 7.17 ppm. This proved the symmetry of the molecule. The rest of the molecule is straightforward. Two overlapping doublets at 7.9 ppm (2H, 1 and 9), 7.6–7.7 (3H, phenyl) multiplet, 7.4 (2H, phenyl) doublet, 7.3–7.31 (2H, 2 and 8) multiplets and 5.9/6.0 (2H, 4 and 6) singlets. High resolution mass spectrometry confirmed the molecular ion.

The chemistry of bis(4-methylphenyl)amine **5** was explored further owing to its facile oxidation. Nitrosation with sodium nitrite in MeOH/H^+ gave *N*-nitroso-bis(4-methylphenyl)amine **8** (Scheme 4). The asymmetry of nitrosated aromatic amines has been reported previously.[20] This compound shows two methyl groups at 2.37 and 2.40 ppm in the ^{1}H NMR and a more complex aromatic region. There are eight aromatic carbons in the ^{13}C NMR. The asymmetry indicates restricted rotation around the *N, N* bond, which must be slow on an NMR time scale.

Compound **8** rearranges into (2-nitro-4-methylphenyl)-4-methylphenylamine **9** when treated with montmorillonite in CH_2Cl_2 at rt. The reaction mixture begins to turn orange within minutes. Presumably the *N*-nitroso group is firstly oxidised to an *N*-nitro group which then migrates to an *ortho* position since the *para* positions are blocked. The product **9** appears as a red solid and has a long wavelength absorption maximum of 441 nm. The structure of **9** was confirmed by a single crystal structure determination (Fig. 2).

Synthesis with N-*methyl*-p-*toluidine* (**10**)

Again we chose to study a modified derivative of *p*-toluidine, *N*-methyl-*p*-toluidine **10** (Scheme 5). The oxidation of *N*-methyl-*p*-toluidine **10** and aniline with $K_2Cr_2O_7$ is a much better reaction than the oxidation of *p*-toluidine and aniline. The reaction turns a deep purple colour within half an hour. Presumably the *N*-methyl group serves to favour the formation of a nitrogen centred radical, as for bis(4-methylphenyl)amine **5**, which then reacts with aniline. This reaction fails using either *N*-methylaniline or *N*-ethylaniline showing that the *p*-methyl group is necessary to favour the oxidation pathway. The product showed a characteristic absorption maximum at 550 nm and an *N*-methyl group at 3.32 ppm in the ^{1}H NMR. Since this peak is close to the resonance for residual MeOH the

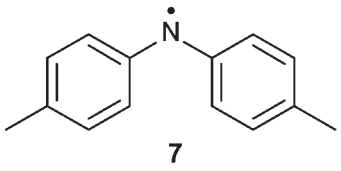
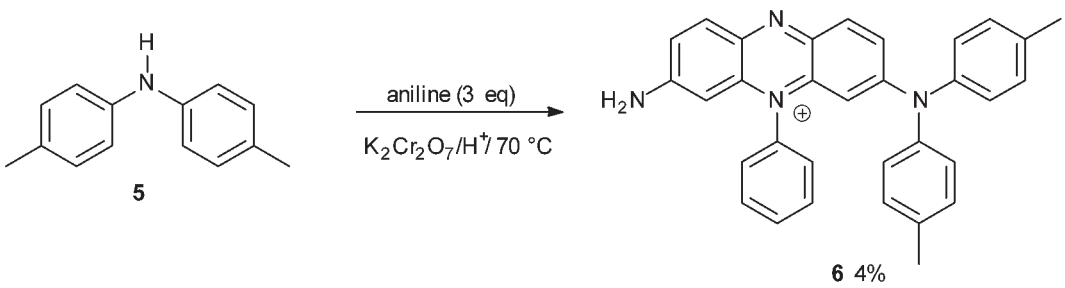
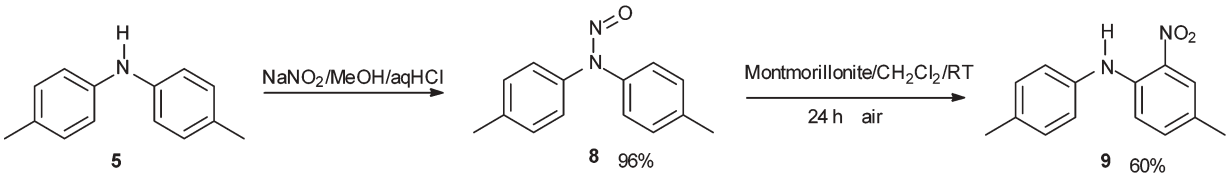


Fig. 1 A possible free radical that might react with aniline by homolytic aromatic substitution.



Scheme 3 The oxidation of bis(4-methylphenyl)amine **5** to give mauveine chromophore derivative **6**.



Scheme 4 The nitrosation of bis(4-methylphenyl)amine and its subsequent rearrangement.

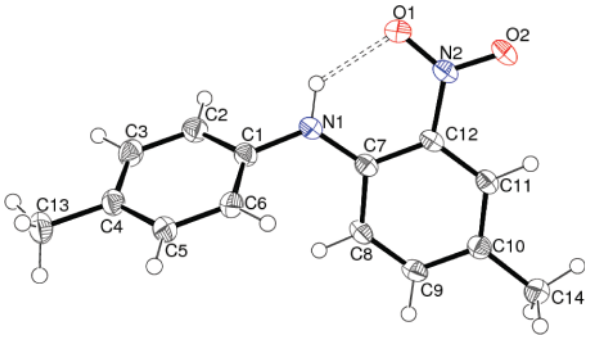
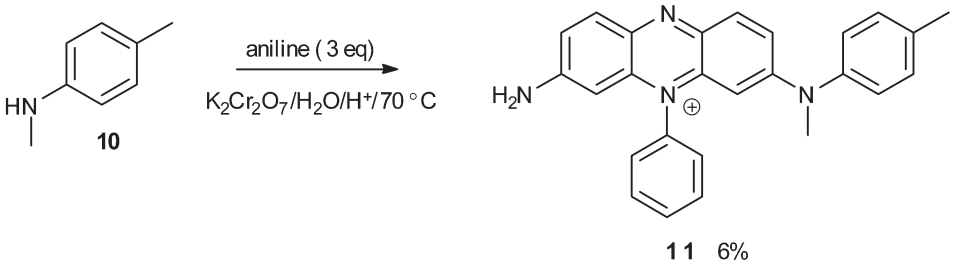


Fig. 2 The molecular structure of **9** showing 50% displacement ellipsoids. The intramolecular N–H···O hydrogen bond [H···O = 1.943 (18) Å; N–H···O = 130.0 (15)°] is shown as a double–dashed line. The dihedral angle between the ring planes is 58.94 (5)° and the nitro group is close to coplanar with its attached ring [dihedral angle = 5.14 (11)°]. The only possible intermolecular interaction in the crystal is a very weak C–H···π bond.

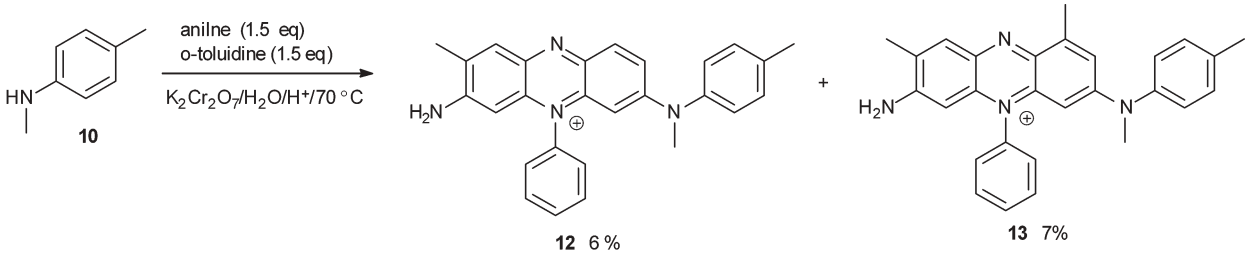
spectrum was run in both CD_3OD and D_2O. Interestingly, in D_2O, the spectrum showed greater resolution and the expected methyl group at 3.0 ppm. The compound is more soluble in water than mauveine chromophores with NH at this position. The ^{13}C NMR showed 22 peaks and had an *N*-methyl resonance at 41.2 ppm. The high resolution mass spectrum showed the correct molecular ion for a structure with the *N*-methyl group. Initially we had thought that the *N*-methyl group might be oxidatively removed during the course of the reaction but it is, in fact, quite robust. We also failed to remove it by oxidation of compound **11** with $K_2Cr_2O_7$ in dilute acetic acid or in dilute H_2SO_4 (1.0 mL in 100 mL H_2O).

This reaction was attempted oxidising *N*-methyl-*p*-toluidine **10** and aniline/*o*-toluidine (Scheme 6) in the same way. As for Scheme 5 this is a much better reaction for making derivatives of mauveine than the oxidation of *p*-toluidine/*o*-toluidine/aniline.

To separate mixtures of mauveine chromophores by column chromatography the counterion was changed from sulfate to acetate. This is easily achieved by taking the dry methanol extract from a reaction, agitating with dilute sodium hydroxide and filtering. The precipitate can be washed with base but pure water immediately begins to redissolve the dye. After base treatment the precipitate is extracted with MeOH, then acidified with a few drops of HOAc and evaporated to dryness. Chromatography is performed using *sec*-butanol/EtOAc/H_2O/HOAc (60:30:9.5:0.5).[11] By this method the two chromophores were separated by collecting fractions and characterised. The yields from reacting *o*-toluidine and aniline with compound **10** are much higher than the yields from using aniline alone. *N*-methylmauveine B **13** elutes first. It gave three methyl groups in the ^{13}C NMR at 16.2, 16.7 and 19.7 ppm. The *N*-methyl group appeared at 39.7 ppm. In the ^1H NMR spectrum, a characteristic singlet was present at 7.81 ppm for the deshielded proton at position 9. The characteristic methyl group at position 1 also appeared deshielded at 2.7 ppm. The high resolution mass spectrum confirmed that the molecular ion. *N*-methylmauveine A **12** elutes next. It showed two methyl groups in the ^{13}C NMR at 16.2 and 19.8 ppm and an *N*-methyl group at 39.8 ppm. The ^1H NMR spectrum showed a characteristic doublet at 7.8 ppm for the proton at position 1 and a singlet at 7.7 ppm for the proton at position 9. High-resolution mass spectrometry confirmed the molecular ion. For both *N*-methylmauveine A and *N*-methylmauveine B, the central



Scheme 5 A novel synthesis of *N*-methyl-C25b from *N*-methyl-*p*-toluidine. (C25b is the name given to the chromophore lacking the *N*-methyl group).[13]



Scheme 6 A novel synthesis of *N*-methylmauveine A **12** and *N*-methylmauveine B **13** from *N*-methyl-*p*-toluidine. (Mauveine A and mauveine B respectively are the names given to the chromophores lacking the *N*-methyl group.[13])

phenyl ring is apparent because three hydrogens appear as a multiplet centred around 7.75 ppm and the two *ortho* protons appear as a doublet further upfield at about 7.4 ppm. Evidently the use of an *N*-alkylated building block favours the incorporation of a phenyl ring into position 5 (aniline as the building block). The IR spectra of both dyes show absorptions at 1550 cm^{-1} and 1408 cm^{-1} due to asymmetric and symmetric C–O stretches respectively.[21] Both dyes show the same absorption maximum at 550 nm and stain silk an attractive purple colour from water. In each case, the *N*-methyl groups are masked behind the CD_3OD. The *N*-methyl groups were not removed by oxidation of purified material with $K_2Cr_2O_7$ in hot dilute aq. H_2SO_4 or in boiling acetic acid with KOAc. The oxidation of *N*-allyl-*p*-toluidine[2] and aniline by Perkin was not successful.

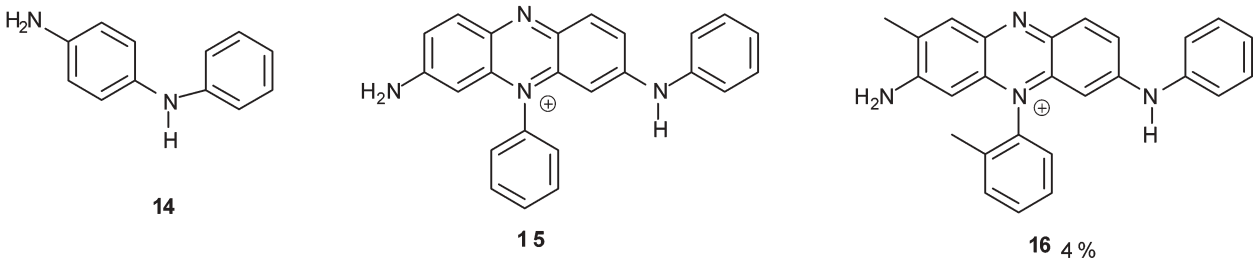
Synthesis with N-*phenyl*-p-*phenylenediamine* (**14**)

Previously we reported the use of *N*-phenyl-*p*-phenylenediamine **14** for the synthesis of pseudo-mauveine **15** and the mauveine A homologue **16** (Scheme 7).[16] We considered that the dimer of aniline[14] might have been used by Perkin as a starting material to make pseudo-mauveine. Here the purification of compound **16** has been improved by careful washing of the final product with water. When mauveine forms it precipitates from water onto the polyaniline by-product. Once purified from this, it is more water soluble so only a small volume of water is used.

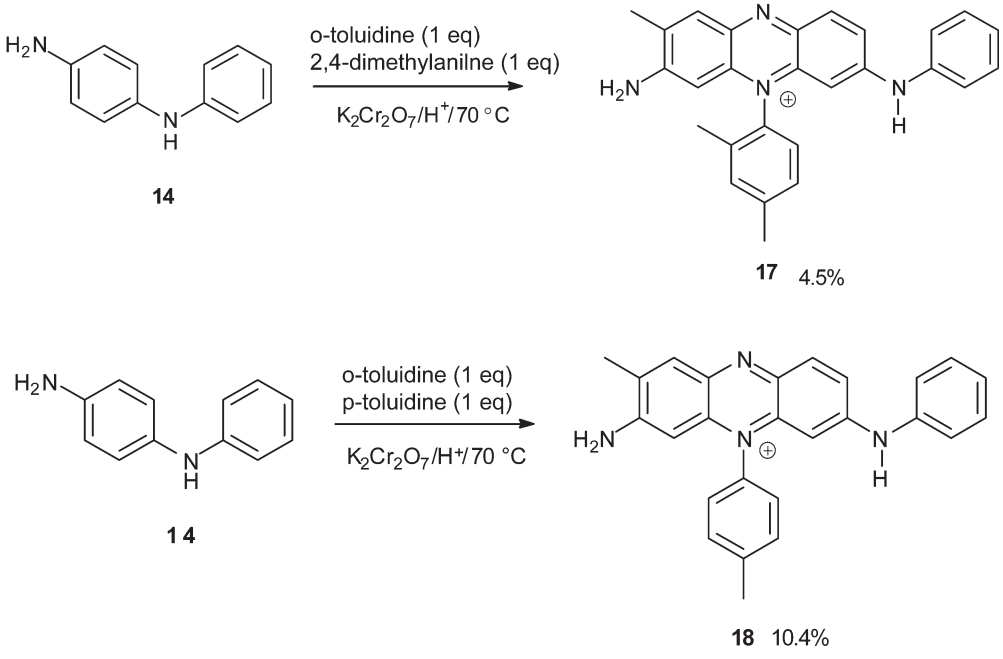
Two more reactions using *N*-phenyl-*p*-phenylenediamine **14** to make mauveine derivatives have been studied. It was mixed with *o*-toluidine and either 2,4-dimethylaniline or *p*-toluidine and then oxidised. The corresponding mauveine A homologues **17** and **18** were fully characterised spectroscopically and are shown in Scheme 8. 2,4-Dimethylaniline was incorporated into a mauveine derivative because it might have been an impurity in Perkin's aniline. Hence a homologue from it might occur in the mauveine archives. The possibility that a xylidine might have been used in mauveine synthesis has been briefly considered owing to the occurrence of small amounts of uncharacterised higher homologues in Perkin's mauveine.[13] *m*-Xylene is the predominant xylene in benzene from coal tar[22] and would lead to 2,4-dimethylaniline by nitration and reduction.

Mauveine synthesis in distilled versus *tap water*

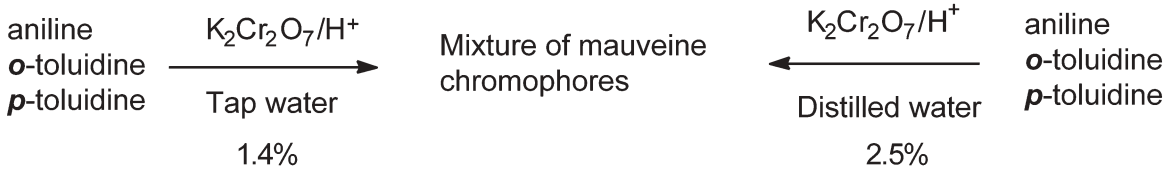
To check if water composition could have an effect on mauveine synthesis, we studied the oxidation of aniline/*o*-toluidine/*p*-toluidine with $K_2Cr_2O_7$ in either tap water or distilled water side by side (Scheme 9). In warm distilled water initially the reaction darkened noticeably faster. Since we have suggested that free radicals may be involved, some metal ions might act as inhibitors to the reaction. In the first few minutes or so, the colour change resembled that seen in the oxidation of *N*-methyl-*p*-toluidine. When purified by chromatography the long mauveine bands looked similar. The product from using distilled water as solvent was dark green, pure and more crystalline. However, the product from using tap water as solvent was darker, amorphous and less pure. The yields were both low as expected (distilled water: 2.5%, tap water: 1.4%). We



Scheme 7 Two mauveine derivatives (**15** and **16**) that can be prepared from *N*-phenyl-*p*-phenylenediamine **14**.[16]



Scheme 8 The synthesis of two new mauveine derivatives from *N*-phenyl-*p*-phenylenediamine.



Scheme 9 A comparison of yields for making mauveine in either distilled water or tap water.

suggest that distilled water is the preferred solvent to use in mauveine syntheses.

Silk dyeing

Pieces of silk were dyed to compare hues and to see if the colour matched that of various museum artifacts dyed with mauveine. Both the samples made using either distilled water or tap water as solvent were purified by chromatography. They both dye silk the same shade of purple, which is duller and bluer[15] than silk dyed from compounds **11–13** and compounds **15–18** (which lack the methyl group of the 4-methylphenylamino group at position 3). This observation on colour was first made by W. H. Cliffe back in 1956. He prepared mauveine by Perkins method but failed to reproduce the red/purple shade of silk he saw with authentic mauveine obtained from Perkin.[15] His mauveine was not purified by chromatography so might have been less pure but our material has been purified by chromatography. With a small sample of Perkin's 1862 authentic mauveine we have also confirmed this observation. This mystery has not yet been solved.

Compounds **11–13** and **15–18** dye silk a bright red shade of purple, which by eye resembles the colour of silk dyed with authentic mauveine and of various museum items dyed with mauveine.[23] Figure 3 compares silk dyed with compounds **12–13** and the mixture of dyes made by Perkin's method. Silk dyed with compounds **15–18** looks similar to silk dyed with compounds **11–13**. Although the absorption maximum is the same at 555 nm compounds **11–13** show a shoulder in the UV-Vis spectrum at 500–530 nm, which may account for the different colour of the dye on silk. Purple consists of red and blue light so absorption of more blue light will give a redder shade of purple. Absorption of more red light would give a bluer shade of purple. A so-called red shade and blue shade of mauveine have been observed before and photographed, although the method of synthesis of the dyes was not stated.[13] Perkin introduced the concept of red and blue shades of mauveine to describe the different shades of purple he obtained from oxidising aniline containing either a large or small amount of toluidines respectively.[5] He published one further synthetic patent after his initial disclosure on mauveine,[1] which involved alkylation studies of mauveine leading to a red shade of mauveine but this method does not appear to have been exploited.[24] An HPLC comparison of Perkin's mauveine with a modern repeat synthesis has shown them to be similar, although mauveine B2 and mauveine C were more dominant in the modern synthesis.[14] In summary a red shade of mauveine on silk may be explained from compounds **12–13** as a consequence of a hypsochromic shoulder on the absorption maximum at 555 nm.

In a further experiment, we treated authentic mauveine with base, filtered the precipitate and changed the counterion to acetate by a standard procedure reported here. The mauveine salt still dyed silk a red shade of mauveine showing that no special anion or additive gives the red mauveine shade.

Characterisation of authentic mauveine

The *N*-methylated compounds **11–13** do not appear to be present in archived mauveine because we checked previous work[11] and analysed an as supplied authentic sample by ^{13}C NMR (CD_3OD). The spectrum showed four strong signals for aromatic methyl groups (17.7, 17.9, 20.9 and 21.0 ppm, one resonance is missing) a strong resonance at 95.0 ppm for carbons 4 and 6, weaker peaks at 93.3 and 94.8 ppm from another chromophore and strong peaks in pairs at 153.4, 153.6, 158.5 and 159.0 ppm indicating two main chromophores to be present. However, there were no *N*-methyl resonances at 39 ppm and no methyl groups from an ethyl group at about 11 ppm. No methyl resonance from an acetate group was present and a carbonyl group was absent. Apart from the aromatic methyl groups the spectrum was free of any peaks from 0 ppm down to 93 ppm. The mass spectrum was very clean showing peaks at 377(3), 391(73), 405(100), 419(49) and 433(9). No other peaks were present. Authentic mauveine separates into two spots on a TLC plate using the eluent *sec*-BuOH/EtOAc/H_2O/HOAc (60:30:9.5:0.5). We purified a small sample and confirmed that the first spot has molecular weights of 405(100), 419(77) and 433(15) then the second spot has molecular weights of 390(100) and 391(94). The methyl group at position 1 will shield *N*-10 reducing the polarity, which explains why the compound of molecular weight 405 elutes first. Compounds **11** and **12** elute as a third more polar spot when co-spotted with archive mauveine.

Conclusions

A novel hydroxylated derivative of pseudo-mauveine has been characterised from an unusual reaction in which the oxidant would have been expected to react with the product. Bis(4-methylphenyl)amine **5** and *N*-methyl-*p*-toluidine **10** are efficient building blocks for the synthesis of derivatives of mauveine chromophores. *N*-Nitroso-bis(4-methylphenyl)amine **8** undergoes a facile rearrangement and oxidation catalysed by montmorillonite. 2,4-Dimethylaniline has been used to make a

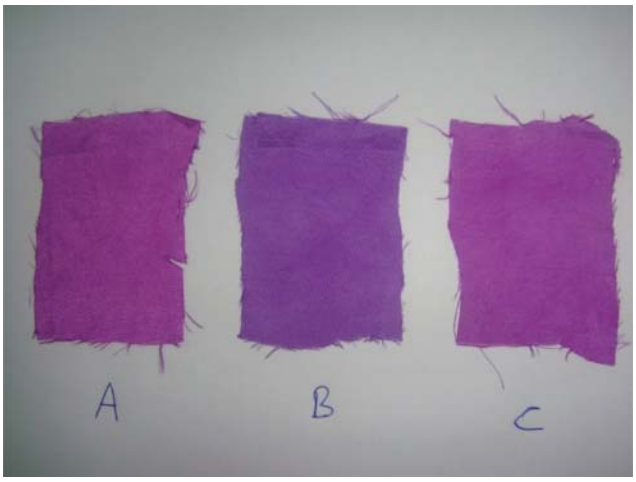


Fig. 3 In each photograph, the purple contrast has changed slightly through photography. (A) Silk dyed with *N*-methylmauveine A **12**. (B) Silk dyed with mauveine made by oxidising aniline and *o*/*p* toluidines in distilled water. (C) Silk dyed with *N*-methylmauveine B **13**.

derivative of a mauveine chromophore. A comparison has been made of the two different shades of silk dyed from mauveine made by oxidising aniline and *o*/*p*-toluidines and by the new routes reported here. They were compared with the shade of silk dyed from a sample of authentic mauveine.

Experimental

UV-Vis spectra were recorded with an Agilent Technologies Cary 60 spectrophotometer. IR spectra were recorded with a Perkin-Elmer FT-IR Spectrum 400 with PIKE Technologies GladiATR diamond anvil or on an ATI Mattson FTIR spectrometer using potassium bromide discs. Melting points were recorded with a Laboratory Devices USA MEL-TEMP II instrument. Mass spectra were recorded by the UK national mass spectrometry service centre with an Orbitrap ASAP. NMR data were recorded using a JEOL model ECA 400 spectrometer. Coupling constants are in Hz. Carbon 13 data acquisition typically requires a 16 h run. Phenosafranin was commercially available from Sigma-Aldrich. Distilled water is recommended as solvent for the mauveine syntheses reported here. Chromatography was performed using flash silica Merck grade 9385 (0.040–0.063 mm), a Coralife Luft Aquarium air pump (5 watts, 7 psi) and a seven star grounded 100 watts stepdown transformer. aqNH_3/MeOH (20:80) was used to elute chromophores with a counterion from a strong mineral acid. *sec*-Butanol/EtOAc/H_2O/HOAc (60:30:9.5:0.5) was used to elute chromophores with an acetate counterion. aqNH_3/MeOH (20:80) cannot be used to elute chromophores with an acetate counterion as they deprotonate and are then too polar. Silk pieces cut from a handkerchief were dyed in hot water (30–50 mL) at 50–60 °C with stirring. Typically about 10–20 mg of chromophore was dissolved but only a small amount was consumed. Stirring increases the rate of absorption of dye onto the silk. CCDC 901034 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

X-Ray crystal structure of compound **9**

The X-ray intensity data for **9** were collected on a Bruker Kappa CCD diffractometer (graphite monochromated MoKα radiation, λ = 0.71073 Å, T = 120 K) with the aid of the COLLECT[25] and DENZO[26] programs. The unit-cell dimensions were obtained by least-squares refinement against the positions of 10010 reflections (2.91° < θ 27.5°). The structure was solved by direct methods with SHELXS-97[27] and the atomic model was refined against $|F|^2$ by full matrix least-squares with SHELXL-97.[27] All the C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding; the N-bound H atom was located in a difference map and its position freely refined [N–H = 0.908 (19) Å]. The refined site occupancies of the O atoms of the nitro group did not differ significantly from unity and were fixed as 1.00 in the final refinement cycles. Red plates of compound **9** were obtained from light petroleum 40–60: dichloromethane (50:50): $C_{14}H_{14}N_2O_2$, M_r = 242.27, crystal dimensions 0.68 × 0.58 × 0.16 mm, triclinic, space group $P\bar{1}$ (No. 2), Z = 2, a = 8.1009 (2), b = 8.1826 (3), c = 9.5700 (4) Å, α = 88.204 (2), β = 80.521 (2), γ = 76.094 (2)°, V = 607.34 (4) Å^3 at 120 K. Number of measured and unique reflections = 12261 and 2787, respectively (R_{int} = 0.034). Final $R(F)$ = 0.051, $wR(F^2)$ = 0.132 for 169 parameters and 2341 reflections with $I > 2\sigma(I)$ (corresponding R-values based on all 2787 reflections = 0.060 and 0.138, respectively), all C-bound H atoms were geometrically placed and refined as riding; the N-bound H atom was located in a difference map and its position freely refined. The refined site occupancies of the O atoms of the nitro group did not differ significantly from unity.

3-(4-Hydroxyphenylamino)-5-phenyl-7-aminophenazinium sulfate (**2**): Phenosafranin (100 mg, 0.3 mmol) and a large excess of aniline (1.5 g, 16 mmol, 50 fold) were dissolved in dilute sulfuric acid (20 ml cH_2SO_4 added to 280 ml of distilled H_2O) in a beaker. The mixture was treated with $K_2Cr_2O_7$ (0.5 g, 1.7 mmol) with stirring and heated at 75 °C for 1 h. The mixture was then cooled and filtered through a fine pore sinter (4–8 μm porosity). The precipitate was washed with H_2O then extracted about 7–8 times with portions of MeOH (40 mL) each time agitating the precipitate on the sinter. The combined MeOH extracts were evaporated to dryness in a beaker on a hotplate followed by flash chromatography on silica gel. MeOH does not elute the product so portions of MeOH can be used to load the product onto the column. MeOH firstly elutes brown impurities. Aqueous cNH_3/MeOH (20/80) then elutes a dark band characteristic of mauveine syntheses followed by the title compound **2** (3.5 mg, 3%) as a purple solid m.p. > 240 °C; λ_{max} (ethanol)/nm 551 (log ε 4.6) and 279 (4.4); ν_{max} (KBr)/cm^{-1} 3305–2108 (br), 1648m, 1603vs, 1489vs, 1381s, 1310s, 1254s, 1075vs (br), 865m, 811m and 605s; δ_H (400 MHz; CD_3OD) 5.99 (1H, d, J = 2.2), 6.13 (1H, d, J = 2.2), 6.70 (2H, d, J = 8.8), 6.9(2H, d, J = 8.8), 7.24 (1H, dd, J = 9.2 and 2.2), 7.35 (1H, dd, J = 9.2 and 2.2), 7.47 (2H, d, J = 7.4), 7.71–7.81 (3H, m), 7.91 (1H, d, J = 9.3) and 7.95 (1H, d, J = 9.3); *m/z* (Orbitrap ASAP) 379.1551 (M^+, 100%) $C_{24}H_{19}N_4O$ requires 379.1553.

3-(N,N-4-Methylphenylamino)-5-phenyl-7-aminophenazinium sulfate (**6**): Bis(4-methylphenyl)amine **5** (250 mg, 1.27 mmol) and aniline (360 mg, 3.87 mmol) were added to distilled H_2O (300 mL) acidified with cH_2SO_4 (six drops, 0.3 mL) in a beaker. Acetone (100–150 mL) was added to dissolves. The beaker was covered with an evaporating plate and heated for 4–5 h with vigorous stirring. The solution was purple because acetone dissolved the dye. Heating was stopped and stirring was continued overnight with the fan on and the lid removed to evaporate the acetone. It is essential to evaporate the acetone prior to filtration. The mixture was filtered through a fine pore sinter (4–8 μm porosity) to leave a precipitate, which was washed with water and then extracted with portions of MeOH (40 mL x 8). The combined extracts were evaporated to dryness in a beaker on a hotplate then purified by flash chromatography on silica gel. The column was loaded by dissolving the product in aliquots of MeOH. MeOH firstly eluted brown impurities and then aqueous cNH_3/MeOH (20/80) eluted a dark band characteristic of mauveine syntheses followed by the title compound **6** (24 mg, 4%) as a purple solid, m.p. > 240 °C; λ_{max} (ethanol)/nm 560 (log ε 4.6) and 283(4.4); ν_{max} (KBr)/cm^{-1} 3328–2107(br), 1589vs, 1502vs, 1463vs, 1372vs, 1316vs, 1281vs, 1175vs, 1128vs, 875m, 813m, 795m, 693m and 478m; δ_H (400 MHz; CD_3OD) 1.88 (3H, s), 2.33 (3H, s), 5.94 (1H, d, J = 2.5), 6.01 (1H, s), 7.07 (4H, d, J = 8.0), 7.18 (4H, d, J = 8.0), 7.27 (1H, d, J = 8 and 2.2), 7.31 (1H, d, J = 9.3), 7.37 (2H, d, J = 7), 7.60–7.68 (3H, m) and 7.95 (2H, d, J = 9.3); δ_C (100.1 MHz; $CDCl_3$) 24.2, 94.7, 100.5, 121.9, 123.9, 127.8, 128.6, 131.7, 131.9, 132.4, 133.9, 135.6, 137.0, 137.4, 137.4, 138.8, 139.0, 140.2, 142.8, 156.1 and 160.0; *m/z* (Orbitrap ASAP) 467.2225 (M^+, 100%) $C_{32}H_{27}N_4$ requires 467.2230.

CAUTION: Suitable precautions should be taken for the preparations of **8** and **9** as nitrosated aromatic amines are carcinogenic.

N-Nitroso-bis(4-methylphenyl)amine (**8**): Bis(4-methylphenyl)amine **5** (2.0 g, 0.01 moles) was dissolved in MeOH (200 mL) containing cHCl (5.0 mL) and was cooled in an ice bath. $NaNO_2$ (1.4 g, 0.02 moles) dissolved in a small amount of H_2O (10 mL) was added in portions with stirring over a few minutes. The reaction was monitored by TLC (25% DCM/75% light petroleum ether 40–60). Additional aliquots of $NaNO_2$ were required to make the reaction go to completion. The product precipitates as a yellow solid. After an arbitrary period of 1 h, water was added (300 mL) and the product collected by suction filtration. To dry the product it was dissolved in CH_2Cl_2, dried over Na_2SO_4, filtered then concentrated *in vacuo* to give the title compound **8** (2.21 g, 96%) as a yellow/orange solid, m.p. 100–100.5 °C; λ_{max} (ethanol)/nm 292 (log ε 3.14) and 206(sh) (4.62); ν_{max} (diamond anvil) 1508s, 1458s, 1410m, 1318m, 1191m, 1168m, 1056vs, 814vs, 793s, 723m, 697m, 614m, 539m, 525s, and 469m; δ_H (400 MHz; $CDCl_3$) 2.34 (3H, s), 2.40 (3H, s), 6.90 (2H, d, J = 8.3), 7.20 (2H, d, J = 8.3), 7.28 (4H, m); δ_C (100.1 MHz; $CDCl_3$) 20.9, 21.2, 119.7, 126.9, 129.8, 130.3, 134.3, 136.9, 139.5 and 140.2; *m/z* (Orbitrap ASAP) 227.1179 (M+H, 100%) and 197 (M+H – NO, 60%) $C_{14}H_{15}N_2O$ requires 227.1179.

(2-Nitro-4-methylphenyl)-4-methylphenylamine (**9**): *N*-Nitroso-bis(4-methylphenyl)amine **8** (200 mg, 0.88 mmol) in CH_2Cl_2 (100 mL) was treated with montmorillonite (2.0 g) in a beaker and left standing at room temperature for 24 h. The solution turned orange after a few minutes. The reaction was filtered and the catalyst was washed with some CH_2Cl_2. The filtrate was concentrated and purified by flash chromatography on silica gel. Light petroleum 40-60:dichloromethane (75:25) eluted the title compound **9** (127 mg, 60%) as red crystals, m.p. 82.0–82.5 °C (from light petroleum: dichloromethane); λ_{max} (ethanol)/nm 441 (log ε 3.6), 259 (3.9), 231 (3.9) and 209 (3.9); ν_{max} (KBr)/cm^{-1} 1629m, 1564s, 1508vs, 1399s, 1339s, 1261vs, 1218vs, 1196vs, 1148vs, 922m, 820vs, 806vs, 764s, 493s and 478vs; δ_H (400 MHz; $CDCl_3$) 2.28 (3H, s), 2.37 (3H, s), 7.90–7.22 (6H, m), 8.00

(1H, s) and 9.40 (1H, s); δ_C (100.1 MHz; $CDCl_3$) 20.2, 21.0, 116.1, 124.4, 125.8, 126.9, 130.3, 132.6, 135.3, 136.3, 137.2 and 141.6; *m/z* (Orbitrap ASAP) 243.1131 (M^+ + H, 100%) $C_{14}H_{15}N_2O_2$ requires 243.1128.

3-[4-Methylphenyl(methylamino)]-5-phenyl-7-aminophenazinium sulfate (**11**): *N*-Methyl-*p*-toluidine **10** (225 mg, 1.86 mmol) and aniline (520 mg, 5.6 mmol) were dissolved in H_2O (200 mL) in a beaker acidified with cH_2SO_4 (six drops, 0.3 mL) followed by the addition of $K_2Cr_2O_7$ (912 mg, 3.1 mmol, 1.67 equiv.). The mixture was stirred and heated at 70–80 °C for 4 h then cooled and filtered through a fine pore (4–8 μm porosity) sinter. The precipitate was washed with H_2O then extracted with portions of MeOH (40 mL x8) each time with agitation in the sinter. The combined extracts were evaporated to dryness by heating in a beaker on a hotplate followed by flash chromatography on silica gel. MeOH elutes brown impurities. 20% cNH_3/MeOH firstly elutes a dark band characteristic for these reactions followed by the title compound **11** (52 mg, 6.3%) as a purple solid, m.p. > 240 °C; λ_{max} (ethanol)/nm 550 (log ε 4.59) and 278 (4.58); ν_{max} (diamond anvil) 3045(br), 1594vs, 1483vs, 1376m, 1332vs, 1185s, 1077vs(br), 872m, 818m, 696m and 608m; δ_H (400 MHz; D_2O) 2.21 (3H, s), 3.09 (3H, s), 5.17 (1H, s), 5.67 (1H, s), 6.67 (2H, d, *J* = 8), 6.70 (2H, d, *J* = 8), 6.87 (1H, d, *J* = 11), 6.92 (1H, d, *J* = 14), 7.05 (2H, d, *J* = 8), 7.30 (1H, d, *J* = 11), 7.44–7.49 (3H, m) and 7.59 (1H, t, *J* = 8 and 7); δ_H (400 MHz; CD_3OD) 2.37 (3H, s), 3.31 (3H, s), 5.82 (1H, s), 5.99 (1H, s), 7.08 (2H, d, *J* = 8), 7.25 (4H, m), 7.46 (2H, d, *J* = 7), 7.74–7.81 (3H, m) and 7.91 (2H, m); δ_C (100.1 MHz; $CDCl_3$) 21.1, 41.2, 94.9, 96.1, 119.9, 123.3, 127.4, 128.7, 132.0, 132.1, 132.7, 134.0, 135.3, 136.9, 137.3, 137.7, 138.9, 139.0, 139.4, 143.8, 156.4 and 159.8; *m/z* (Orbitrap ASAP) 391.1920 (M^+, 100%) $C_{26}H_{23}N_4$ requires 391.1917.

3-[4-Methylphenyl(methylamino)]-5-phenyl-7-amino-8-methylphenazinium acetate (*N*-Methylmauveine A) (**12**) and *1-Methyl-3-[4-methylphenyl(methylamino)]-5-phenyl-7-amino-8-methylphenazinium acetate* (*N*-Methylmauveine B) (**13**): *N*-Methyl-*p*-toluidine (250 mg, 2.10 mmol), aniline (326 mg, 3.50 mmol, 1.5 equiv.) and *o*-toluidine (375 mg, 3.50 mmol, 1.5 equiv.) were dissolved in H_2O (200 mL) in a beaker acidified with cH_2SO_4 (six drops, 0.3 mL) followed by the addition of $K_2Cr_2O_7$ (1.15 g, 3.1 mmol, 1.67 equiv.). The mixture was stirred and heated at 70–80 °C for 3 h then cooled and filtered through a fine pore (4–8 μm porosity) sinter. The precipitate was washed with H_2O then extracted with portions of MeOH (40 mL × 8) each time with agitation in the sinter. The combined extracts were evaporated to dryness by heating in a beaker on a hotplate. The material was stirred with aqueous NaOH (5.0 g in water 200 mL) then filtered and washed with aqueous alkali (water begins to redissolve the dyes). The precipitate was then washed with MeOH (50 mL × 4), and the filtrate acidified with HOAc (five drops) and evaporated to dryness. The material was taken up in *sec*-butanol and purified by flash chromotagraphy on silica gel (fractions were collected). Elution with *sec*-butanol/EtOAc/H_2O/HOAc (60:30:9.5:1) gave firstly the title compound *N*-methylmauveine B **13** (59 mg, 6%) followed by the title compound *N*-methylmauveine A **12** (68 mg, 7%) as dark purple solids. *N*-methylmauveine B λ_{max} (ethanol)/nm 550 (log ε 4.76) and 280 (4.75); ν_{max} (diamond anvil) 3326(br), 1545(vs), 1407(vs), 1348(vs), 1017(m) and 645(m); δ_H (400 MHz; CD_3OD) 1.87 (CH_3CO_2), 2.35 (6H, s), 2.70 (3H, s), 5.67 (1H, d, *J* = 2.0), 6.04 (1H, s), 7.05 (2H, d, *J* = 8.2), 7.10 (1H, s), 7.23 (2H, d, *J* = 7.8), 7.42 (2H, d, *J* = 7.0), 7.71–7.78 (3H, m) and 7.85 (1H, s); The *N*-Me resonance is masked by the CD_3OD. δ_C (100.1 MHz; $CDCl_3$) 16.2, 16.8, 19.8, 22.9 ($\underline{C}H_3CO_2$), 39.7, 93.2, 93.7, 118.0, 126.0, 127.4, 129.9, 130.6, 130.7, 131.2, 132.6, 135.5, 135.9, 136.1, 136.4, 136.7, 137.9, 141.9, 142.5, 154.5, 157.6 and 179.0 ($CH_3\underline{C}O_2$); *m/z* (Orbitrap ASAP) 419.2223 (M^+, 100%) $C_{28}H_{27}N_4$ requires 419.2230. *N*-methylmauveine A λ_{max} (ethanol)/nm 550 (log ε 4.65) and 280 (4.62); ν_{max} (diamond anvil) 3311(br), 1551(vs), 1408(vs), 1017(m) and 651(m); δ_H (400 MHz; CD_3OD) 1.87 (CH_3CO_2), 2.35 (6H, s), 5.81 (1H, d, *J* = 3.0), 6.06 (1H, s), 7.05 (2H, d, *J* = 8.2), 7.23 (3H, d, *J* = 8.0), 7.44 (2H, d, *J* = 7.0), 7.70–7.78 (3H, m), 7.83 (1H, s) and 7.92 (1H, d, *J* = 9.6); The *N*-Me resonance is masked by the CD_3OD. δ_C (100.1 MHz; $CDCl_3$) 16.3, 19.8, 22.9 ($\underline{C}H_3CO_2$), 39.8, 93.7, 96.6, 118.6, 126.1, 127.3, 130.6, 130.7, 130.8, 131.3, 132.3, 132.4, 135.5, 135.7, 136.4, 136.4, 137.7, 138.0, 142.5, 154.7, 157.9 and 179.2 ($CH_3\underline{C}O_2$); *m/z* (Orbitrap ASAP) 405.2074 (M^+, 100%) $C_{27}H_{25}N_4$ requires 405.2074.

Attempted oxidation of N-methylmauveine A and B

The mixture of *N*-methylmauveine A **12** and *N*-methylmauveine B **13** (15 mg, 0.04 mmol) in aqueous H_2SO_4 (0.25 mL H_2SO_4: 100 mL H_2O) was heated to 50 °C and treated with $K_2Cr_2O_7$ (100 mg, 0.34 mmol) for 15 min. After cooling the solution it was treated with dil. NaOH to precipitate the product. This was filtered, extracted with MeOH and acidified with HOAc (five drops) then evaporated to dryness in a beaker on a hotplate. The product had identical spectroscopic properties to the starting material including accurate mass molecular ions and the ^{13}C spectrum. A similar method was done in aq HOAc (20 mL HOAc: 80 mL H_2O) giving the same result.

3-Phenylamino-5-(2-methylphenyl)-7-amino-8-methylphenazinium sulfate (**16**): See general method used here and a previous paper for other experimental data.[16] The product was carefully washed with a small volume of cold water (4%); δ_H (400 MHz; CD_3OD) 1.92 (3H, s), 2.40 (3H, s), 6.05 (1H, s), 6.30 (1H, s), 7.13 (3H, m), 7.28 (2H, m), 7.40 (1H, d, *J* = 7.0), 7.47 (1H, d, *J* = 9.0), 7.65 (3H, m), 7.84 (1H, s) and 8.0 (1H, d, *J* = 9.0); δ_C (100.1 MHz; $CDCl_3$) 16.8, 17.6, 94.3, 94.5, 122.0, 123.3, 126.6, 128.7, 130.3, 130.6, 132.3, 132.5, 133.9, 133.9, 134.6, 136.4, 136.8, 136.9, 137.5, 139.2, 140.1, 154.0 and 159.7 (one resonance is missing).

The acetate salts of compounds **17** and **18** for ^{13}C spectra were synthesised as for compounds **12** and **13**

3-(Phenylamino)-5-(2,4-dimethyphenyl)-7-amino-8-methylphenazinium sulfate (**17**): *N*-Phenyl-*p*-phenylenediamine (250 mg, 1.36 mmol), *o*-toluidine (145 mg, 1.36 mmol) and 2,4-dimethylaniline (164 mg, 1.36 mmol) were dissolved in distilled H_2O (250 mL) treated with CH_2SO_4 (six drops, 0.3 mL). The mixture was treated with $K_2Cr_2O_7$ (535 mg, 1.82 mmol, 1.34 equiv.) and stirred at 70 °C for 5 h. The mauve-coloured reaction mixture was then cooled and filtered through a fine pore sinter (4–8 μm porosity). The precipitate was washed with H_2O, then extracted with MeOH (40 mL × 8) on the sinter. The combined extracts were evaporated to dryness in a beaker on a hot plate then purified by flash chromatography on silica gel (2–3 fractions were collected and analysed by TLC). MeOH elutes impurities then 20% cNH_3/MeOH elutes a dark band followed by the title compound **17** (27.8 mg, 4.5%) as a purple solid, m.p. > 240 °C (from suspending in a small volume of water and filtration) λ_{max} (ethanol)/nm 553 (log ε 4.6), 281 (4.5), 231 (4.2) and 204 (4.4); ν_{max} (KBr)/cm^{-1} 3500–2100 (br), 1608vs, 1589vs, 1529vs, 1493vs, 1463vs, 1343vs, 1307vs, 1182vs, 1135vs, 1098vs, 1012s, 825m, 753m, 717m, 693m and 610m; δ_H (400 MHz; CD_3OD) 1.87 (3H, s), 2.37 (3H, s), 2.48 (3H, s), 6.08 (1H, s), 6.32 (1H, s), 7.14 (3H, m), 7.25 (1H, d, *J* = 7.6), 7.28 (3H, m), 7.41 (1H, d, *J* = 7.6), 7.47 (1H, s), 7.84 (1H, s) and 8.00 (1H, d, *J* = 9.2); δ_C (100.1 MHz; $CDCl_3$) (acetate salt) 16.7, 17.6, 21.3, 24.2 ($\underline{C}H_3CO_2$), 94.4, 94.8, 121.7, 123.2, 126.6, 128.4, 130.6, 130.7, 132.4, 133.7, 133.9, 134.3, 134.6, 135.9, 137.0, 137.1, 137.5, 139.3, 140.0, 143.1, 153.9, 159.6 and 180.5 ($CH_3\underline{C}O_2$); *m/z* (Orbitrap ASAP) 405.2073 (M^+, 100%) $C_{27}H_{25}N_4$ requires 405.2074.

3-(Phenylamino)-5-(4-methylphenyl)-7-amino-8-methylphenazinium sulfate (**18**): *N*-Phenyl-*p*-phenylenediamine (250 mg, 1.36 mmol), *p*-toluidine (145 mg, 1.36 mmol) and *o*-toluidine (145 mg, 1.36 mmol) were dissolved in distilled H_2O (250 mL) treated with cH_2SO_4 (six drops, 0.3 mL). The mixture was treated with $K_2Cr_2O_7$ (535 mg, 1.82 mmol, 1.34 equiv.) and stirred at 70 °C for 5 h. After 30 min the reaction stains silk brown but after 1.5 h it stains silk purple. The mauve coloured reaction was then cooled and filtered through a fine pore sinter (4–8 μm porosity). The precipitate was washed with H_2O, then extracted with MeOH (40 mL x 8) on the sinter. The combined extracts were evaporated to dryness in a beaker on a hotplate then purified by flash chromatography on silica gel (two or three fractions were collected and analysed by TLC). MeOH elutes impurities then 20% cNH_3/MeOH elutes a dark band followed by the title compound **18** (62 mg, 10.4%) as a purple solid, m.p. > 240 °C (from suspending in a small volume of water and filtration). λ_{max} (ethanol)/nm 555 (log ε 4.7) and 280 (4.7); ν_{max} (KBr)/cm^{-1} 3176s, 3036s, 1665m, 1610m, 1591m, 1434vs, 1062vs(br), 983s, 710m and 609vs; δ_H (400 MHz; CD_3OD) 2.35 (3H, s), 2.51 (3H, s), 6.11 (1H, s), 6.34 (1H, s), 7.12 (3H, m), 7.31 (2H, t, *J* = 8 and 8), 7.35 (2H, d, *J* = 8), 7.38 (1H, d, *J* = 7), 7.59 (2H, d, *J* = 8), 7.78 (1H, s) and 7.92 (1H, d, *J* = 9); δ_C (100.1 MHz; $CDCl_3$) (acetate salt) 17.6, 21.3, 24.2 ($\underline{C}H_3CO_2$) 95.1, 95.5, 121.5, 123.1, 123.3, 126.5, 128.5, 129.9, 130.6, 132.1, 132.2, 133.0, 133.6, 134.4, 135.1, 137.6, 139.2, 142.9, 153.4, 159.2 and 180.0 ($CH_3\underline{C}O_2$); *m/z* (Orbitrap ASAP) 391.1920 (M^+, 100%) $C_{26}H_{23}N_4$ requires 391.1917.

Oxidation of aromatic amines in tap water or distilled water. Aniline (174 mg, 1.87 mmol), *o*-toluidine (200 mg, 1.87 mmol) and *p*-toluidine (200 mg, 1.87 mmol) in either distilled water (250 mL) or

tap water (250 mL) each acidified with cH_2SO_4 (six drops, 0.3 mL) was heated to 75 °C and treated with $K_2Cr_2O_7$ (917 mg, 3.12 mmol, 1.67 equiv.) for 3 h. Each mixture was cooled and filtered. The precipitate was extracted with MeOH (40 mL x 5), evaporated in a beaker, then purified by chromatography. Elution with MeOH gave some brown impurities then 20% cNH_3/MeOH elutes a dark band followed by a long purple band of mauveine chromophores (20 mg, 2.5%) from using distilled water as solvent and (12 mg, 1.4%) from using tap water as solvent.

The exchange of mauveine counterions

See the general procedure for compounds **12** and **13**. For smaller quantities of material the material on a sinter was not washed with aqueous alkali.

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