

## What did W. H. Perkin Actually Make when He Oxidised Aniline to Obtain Mauveine?

Otto Meth-Cohn\* and Mandy Smith†

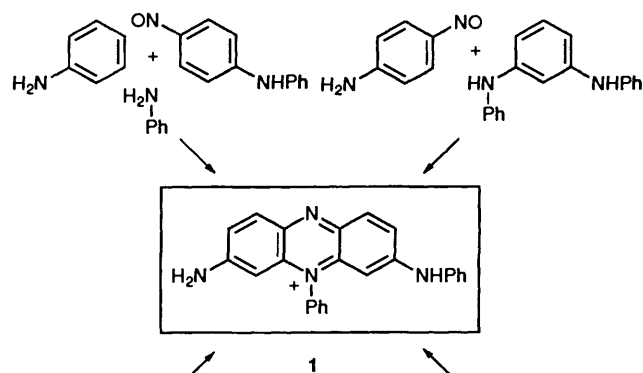
Chemistry Department, University of Sunderland, Sunderland SR1 3SD, UK

The literature structure for mauveine has been shown to be wrong. Analysis of samples of mauveine made by Perkin in his factory show them to be primarily a mixture of two phenazinium dyes, 3-amino-2-methyl-5-phenyl-7-(*p*-tolyl)phenazinium acetate and 3-amino-2,9-dimethyl-5-phenyl-7-(*p*-tolyl)phenazinium acetate

In 1856 William Henry Perkin at the age of 18 years, endeavoured to make quinine by oxidative dimerisation of *N*-allyltoluidine (mostly *para*) with potassium dichromate. The synthesis of quinine was not achieved for a further 88 years.<sup>1</sup> However, when he similarly oxidised 'aniline' (derived from crude coal-tar benzene and thus containing toluene) he obtained a black precipitate from which he was able to extract a purple dye in about 5% yield. This dye became known as mauveine and was sold as an acetate salt. This remarkable event signalled the birth of the dyestuffs industry and indeed the chemical industry.

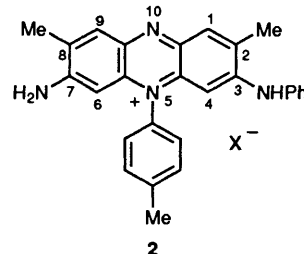
Perkin established that a similar dye was obtained by oxidation of toluidines, xylydines and other anilines and that his original impure aniline gave a better dye than that obtained from pure aniline. This latter product was named pseudo-mauveine from which he showed that mauveine was derived from a base of formula  $C_{27}H_{24}N_4$ . He concluded that mauveine was a mixture of pseudomauveine (to which he gave the structure of the parent base  $C_{24}H_{20}N_4$ ) and a trimethyl derivative derived from *p*-toluidine and aniline.<sup>2</sup>

*The Literature Structure of Mauveine.*—The structure of pseudomauveine **1** was established by Fischer and Hepp<sup>3</sup> and by Nietzki<sup>4</sup> by synthesis in several ways. These involved oxidative couplings as outlined in Scheme 1. However, the



Scheme 1 Synthetic methods for pseudomauveine

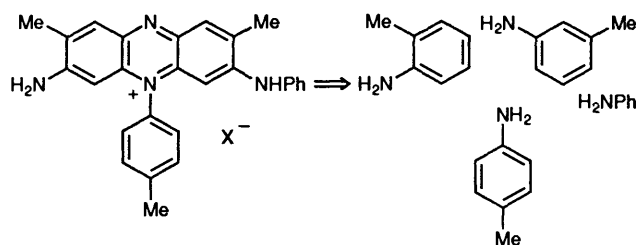
literature structure for mauveine **2** emerged without any indication of proof. It appears in *Chemical Abstracts* (the first appearance referring to Volume 72, in 1970),<sup>5</sup> and in the dyers definitive bible, *The Colour Index* from its first edition in 1924 to date.<sup>6</sup> Beilstein does not give a structure,<sup>7</sup> *Comprehensive*



*Heterocyclic Chemistry* gives two different ones<sup>8</sup> and the definitive Weissberger volume on *Phenazines* correctly quotes the empirical formula of Perkin but presents yet another erroneous structure.<sup>9</sup> A recent review on phenazine dyes refers to the structure **2**<sup>10</sup> while the latest definitive work on the history of dyeing attributes the same erroneous structure to Fischer and Hepp, a commonly accepted fallacy.<sup>11</sup>

### Results and Discussion

Given that mauveine is made by oxidation of crude aniline derived by nitration and reduction of a benzene-toluene mixture, it is clear that the literature structure cannot be correct in that it implies that *m*-toluidine is a key requirement (Scheme 2).



Scheme 2 A retrosynthetic analysis of the literature structure of mauveine

We therefore obtained a sample of mauveine produced in Perkin's factory from the Perkin collection at Zeneca ‡ as well as another sample from the British Museum (donated by Imperial College and probably deriving from Hofmann's collection). Perkin commented on the dyes amazing stability and other workers examining a sample of the 1856 dye almost 100 years later noted that it was unchanged.<sup>5b</sup> We were surprised to discover that the dye gave essentially the same

† In partial fulfilment of the requirements for the B.Sc. degree of Sunderland University.

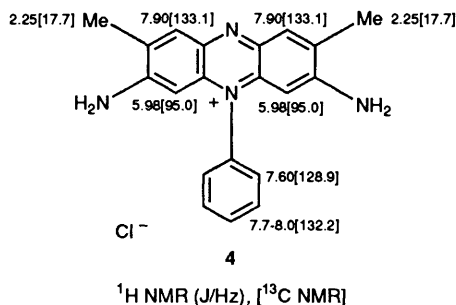
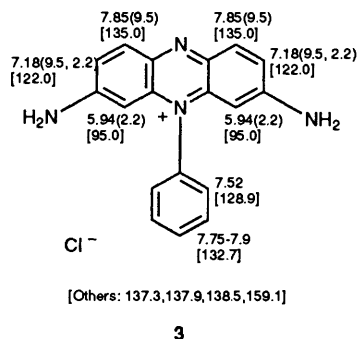
‡ Thanks to Mr Ken McGee for help in obtaining this compound.

combustion analysis data as Perkin recorded. Chemists who examined a sample of Perkin's material 57 years later found that it lost 16.1% weight at 110 °C, mostly water, while Perkin rigorously dried his material prior to analysis.<sup>13</sup>

A direct insertion mass spectrum confirmed the presence of several of the methylated homologues of pseudomauveine, the di- and tri-methyl derivatives giving the largest molecular ions together with small peaks for the mono- and tetra-methyl analogues.

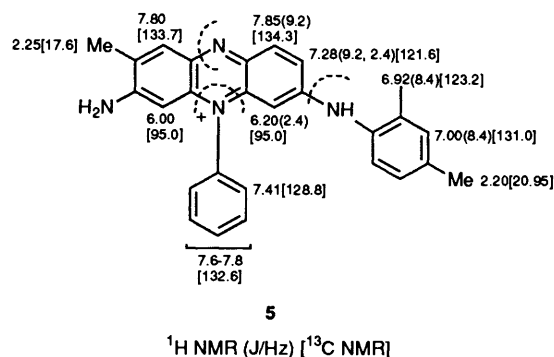
Thin layer chromatography on silica was most effectively conducted utilising a mixture of isobutyl alcohol, 10% aqueous acetic acid and ethyl acetate (6:1:3, v/v) and revealed two major products **A** and **B**,  $R_f$  values 0.45 and 0.52, respectively, as well as some very minor purple dyes. Flash chromatography on silica gel using the same eluent with rechromatography of the two major fractions gave two fairly pure purple dyes.

**Standards to Help Elucidate the Mauveine Structure: Phenosafranin and Safranin O.**—In order to help elucidate the structures we also examined the spectra of two commercially available standards, phenosafranin **3** and safranin O **4** (both from Aldrich, the latter being rather impure despite its claimed ~95% purity). The symmetry of the standards allowed ready assignment of their NMR spectra by use of HH-COSY and HC-COSY spectroscopy and further decoupling studies.



**Structure of the mauveine component A** ( $R_f$  0.45) **5**. By a similar study of the 1- and 2-D NMR spectra and the coupling data we now assign the structure of this major component of mauveine as the acetate salt of **5**. This molecule can be seen to derive from 2 molecules of aniline, 1 of *p*-toluidine and 1 of *o*-toluidine. Noteworthy, in the spectra are the signals to very high field of the 4/6 nuclei both in the standards and the mauveine component A due to the shielding effects of the orthogonal phenyl group and the amino substituents at the 3- and 7-positions.

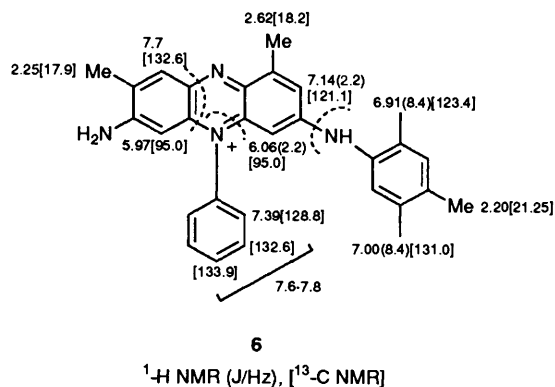
These nuclei are non-equivalent in the mauveine component, one signal showing *meta*-coupling and the other not, thus indicating the position of one of the methyl substituents. This is supported by the presence of only one proton at ~7.21/122 ppm in the proton and carbon spectra, respectively. The extra



*para*-coupled protons clearly indicate the position of the other methyl substituent in the *N*-phenyl ring. The lower field proton signals of the 2- and 4-protons of component A compared to those of phenosafranin due to the deshielding effect of the *N*-phenyl ring supports the relative disposition of the two methyl substituents.

Phenosafranin shows a mass spectral molecular ion for the cation ( $m/z$  287) and a larger one for the radical cation of the neutral species,  $M - 1$ . Strong peaks are evident at  $m/z$  273 ( $M - N$ , the 10-nitrogen) and  $m/z$  196 ( $M - NPh$ ). The mass spectrum of component A conforms to the above structure showing the molecular ion as the base peak ( $m/z$  390) and the next strongest peak ( $m/z$  284) for the  $M - MeC_6H_4NH$  ion. In support of this fragmentation a peak at  $m/z$  106 is significant for the ion  $MeC_6H_4NH^+$ .

**Structure of the mauveine component B** ( $R_f$  0.52) **6**. The mass spectral and NMR data confirms that the second component is very similar to the first but contains an extra methyl group. That this group is in the 1-position and the others are as in component A is evident from the very close similarity in the spectra *except for the absence of the characteristic 1-proton/carbon signals and the ortho-coupling of the 2-proton* (cf. spectra for **5** and **6**). It is also clear that this minor component derives



from 1 molecule of aniline, 1 of *p*-toluidine and 2 molecules of *o*-toluidine. As was recognised by the early chemists involved with mauveine, *o*-toluidine and *p*-toluidine are vital for the formation of the most effective dye and are clearly significantly more reactive in the oxidative coupling process.

## Experimental

**General Details.**—Phenosafranin and safranin O were obtained from Aldrich and used as supplied. Samples of mauveine were obtained from the Perkin Collection, Zeneca p.l.c., Blackley, Manchester and from The Science Museum. Silica gel thin-layer was performed using Merck 0.2 ×

200 × 200 mm precoated plates (Art. 5735) and flash chromatography was conducted with silica from Janssen (0.035–0.070 mm). NMR spectra were recorded on a JEOL GSX 270 using [<sup>2</sup>H<sub>4</sub>]methanol as solvent relative to internal tetramethylsilane. Mass spectra were recorded on a VG Trio 2000 Quadrupole instrument by direct insertion. Microanalytical data were provided by Medac Ltd, Brunel University.

**Mauveine.**—The material was examined as supplied. Chromatography was conducted using isobutyl alcohol–ethyl acetate–aqueous acetic acid (5%, v/v) in the ratio 60:30:10 (v/v). The two different samples gave identical results. Flash chromatography was conducted on 0.1 g samples and the two main fractions were rechromatographed separately using the same solvent system and the material obtained was dried thoroughly in a vacuum oven at 50 °C prior to examination (Found: C, 67.2; H, 6.3; N, 10.8. Calc. for [C<sub>27</sub>H<sub>25</sub>N<sub>4</sub>]<sup>+</sup>·[CH<sub>3</sub>CO<sub>2</sub>]<sup>-</sup>·3H<sub>2</sub>O, C, 67.16; H, 6.61; N, 10.80%). The spectral details are recorded in the Discussion.

### Acknowledgements

We thank Zeneca Specialities and the Science Museum for samples of mauveine, Mr. Ken McGee, archivist of Zeneca Specialities for very helpful discussions and Mr. Peter Kirkpatrick, Perkin's grandson, both for his wholehearted support in conducting this study and useful background material.

### References

- 1 R. B. Woodward and W. von E. Doering, *J. Am. Chem. Soc.*, 1944, **66**, 849.
- 2 W. H. Perkin, *J. Chem. Soc.*, 1896, **69**, 596 and references cited therein.
- 3 O. Fischer and E. Hepp, *Chem. Ber.*, 1888, **21**, 2617; 1893, **26**, 1194; *Liebigs Ann Chem.*, 1892, **272**, 306.
- 4 R. Nietzki, *Chem. Ber.*, 1896, **29**, 1442.

- 5 (a) *Chem. Abstr.*, 1925, **9**, 2567 (ref. to A. Cobenzl, *Oesterr. Chem-Ztg.*, 1925, **28**, 25). It is of interest that this author recognised that mauveine incorporated 2 molecules of *o*-toluidine, 1 of *p*-toluidine and 1 of aniline. (b) First appearance of structure: *Chem. Abstr.*, 1965, **72**, 28258a [ref. to E. Gurr, *J. Soc. Dyers Colour.*, 1969, **85**(10), 473. This paper does not contain the structure and neither does the abstract! However the structure of mauveine appears as 'Phenazinium 3-amino-7-anilino-2,8-dimethyl-5-*p*-tolyl, sulphate' in the 8th Decennial Index and refers to this paper.]
- 6 Dye number 50245, *The Colour Index*, 3rd edn., 2nd revision, Soc. Dyers & Colourists, Bradford, 1992. In the first edition of 1924 mauveine was entry 846.
- 7 *Beilsteins Handbuch der Organischen Chemie*, Verlag von J. Springer, Berlin, 1929, **12**, 131; **25**, 397 (654); System number 1598.
- 8 *Comprehensive Heterocyclic Chemistry*, editors-in-chief A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 1, 318; vol. 3, 197.
- 9 G. A. Swan and D. G. L. Felton, *Phenazines, Chemistry of Heterocyclic Compounds*, ed. E. Weissberger, J. Wiley & Sons, New York, 1957, 159.
- 10 N. Hughes, *Phenazine, Oxazine, Thiazine and Sulphur Dyes, Rodd's Chemistry of Carbon Compounds*, vol. IV, eds. S. Coffey and M. F. Ansell, 2nd edn., 1988, 403.
- 11 A. S. Travis, *The Rainbow Makers—The Origins of the Synthetic Dyestuffs Industry in Western Europe*, Lehigh University Press, Bethlehem, 1993, 268. It appears that the literature structure was invented by Gustav Schulz who was the first to produce a comprehensive Index of all the known dyes in his *Farbstofftabellen*, a work that predated and formed the basis of the *Colour Index*.<sup>12</sup>
- 12 G. Schultz, *Farbstofftabellen*, Akademische Verlagsgesellschaft MBH, Leipzig, 7th edn., 1931, vol. 1, 419 (entry 971). This is the earliest edition of Schultz found during this work. However the structure does not appear in *A Systematic Survey of the Organic Colouring Matters*, 2nd edn., by A. G. Green (founded on the German of G. Schultz and P. Julius), 1904, 232 (dye number 593).
- 13 E. Hibbert, *J. Soc. Dyers Colour.*, 1921, **37**, 187.

Paper 3/04873J

Received 11th August 1993

Accepted 20th September 1993