

Electronic Supplementary Information (ESI)

The synthesis of mauve dyes was made according to the method of Scaccia *et al.*¹ The mixture obtained was analyzed by HPLC-DAD (ThermoFinnigan Surveyor, PDA 5), using a RP-18 analytic column (250/4.6nucleosil 300-5 C18) with an acidic water (pH=1.5):methanol gradient². A historical sample (from the Science Museum, London, ref. n. 1952-175)³ was also analyzed to aid comparison with the products of the modern synthesis. The chromatograms for the two samples are shown in Fig. 1 of the manuscript. The structures of compounds corresponding to peaks **1** and **5** were not yet fully identified and are the topic of an ongoing study.

The peak marked as **1** is a red-coloured fraction ($\lambda_{\text{max(HPLC-DAD)}} = 518 \text{ nm}$) and has not yet been characterized. Fractions corresponding to the peaks numbered from **2** to **6** are all violet in colour ($\lambda_{\text{max(HPLC-DAD)}} \approx 550 \text{ nm}$). The major violet compounds of the synthesized sample, corresponding to peaks **2**, **3**, **4** and **6** were isolated by HPLC-DAD and characterized by UV-Vis spectroscopy, ¹H RMN and mass spectrometry, as shown in Table S1.

Table S1 - MS and NMR data for compounds corresponding to peaks **2**, **3**, **4** and **5** in the chromatogram of Fig. 1 of the manuscript.

	2	3	4	6
FD MS*	391.2 (calc. for	405.2 (calc. for	405.2 (calc. for	419.2 (calc. for
<i>m/z</i>	C ₂₆ H ₂₃ N ₄ ⁺ : 391.2)	C ₂₇ H ₂₅ N ₄ ⁺ : 405.2)	C ₂₇ H ₂₅ N ₄ ⁺ : 405.2)	C ₂₈ H ₂₇ N ₄ ⁺ : 419.2)
¹ H NMR**				
δ /ppm				
$\lambda_{\text{max}}^{\#}$ /nm	551	547	547	546
Name [§]	Mauveine A	Mauveine B2	Mauveine B	Mauveine C
Formula	C ₂₆ H ₂₃ N ₄ ⁺	C ₂₇ H ₂₅ N ₄ ⁺	C ₂₇ H ₂₅ N ₄ ⁺	C ₂₈ H ₂₇ N ₄ ⁺
Year	1994 ⁴	2006	1994 ⁴	2006

*FD MS spectra obtained in a Micromass GC-TOF spectrometer.

**Spectra in CD₃OD obtained on a Bruker AMX400 operating at 400.13 MHz. Assignment is made on the basis of COSY spectra, relative proximity to amino groups and by comparison with the data published by Meth-Cohn and Smith, see ref. 4. In particular, a detailed analysis of the position of the methyl groups in our spectra and comparison with data from ref. 4 allowed to assign to carbon C2 (instead of C9) the position of one of the methyl groups in Mauveine B2. Larger amounts of products are being isolated in order to run ¹³C NMR spectra.

UV-Vis absorption maxima obtained during the HPLC-DAD run.

§ The names are in accordance with those introduced by Meth-Cohn and Smith in 1994 for Mauveine A and Mauveine B (ref. 4). The compound corresponding to peak **3** was named Mauveine B2 since it is an isomer of Mauveine B; the compound corresponding to peak **6** was named Mauveine C.

¹ R. L. Scaccia, D. Coughlin and D. W. Ball, *J. Chem. Educ.*, **1998**, 75, 769-770.

² K. V. Castele, H. Geiger, R. de Loose and C. F. van Sumere, *J. Chromatogr.*, **1983**, 259, 291-300.

³ Obtained from Peter J. T Morris (Science Museum); further details will be presented elsewhere.

⁴ O. Meth-Cohn and M. Smith, *J. Chem. Soc., Perkin Trans. I*, **1994**, 5-7.