

Some Traditional Colourants of Maori and other Cultures

Gerald Smith^a and Rangi Te Kanawa^b

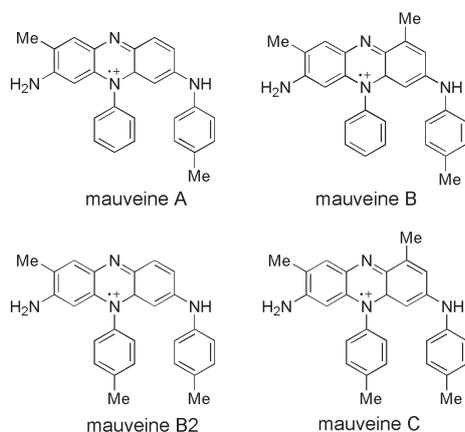
^aSchool of Chemical and Physical Sciences, Victoria University of Wellington and ^bConservation Department, Te Papa, Wellington (e-mail: gerald.smith@vuw.ac.nz)

A Global History of Dyes and Pigments

We live in a world of colour. Today, materials can be decorated in an almost limitless range of colours. The colourants used come in two forms; either as dyes or pigments. Dyes are water soluble chemicals whereas pigments are fine, coloured particles dispersed in a liquid medium which 'dries' after application to the substrate, *i.e.* it solidifies by polymerization, gelation or protein denaturation and *not* by evaporation of the solvent.

The explosion in the number of colourants was due to the advent of synthetic chemistry and the person often credited with being the father of modern organic chemistry is William Perkin who, in 1856, synthesized a mauve dye from aniline which is a component of coal tar. It was known as *mauveine*, as aniline purple, and Perkin's mauve. The actual structure of the dye proved difficult to determine and was confirmed only in 1994 to be a mixture of four related aromatics differing only in the number and location of the methyl groups (Chart 1).¹

Chart 1. The structures that comprise mauveine



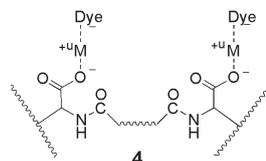
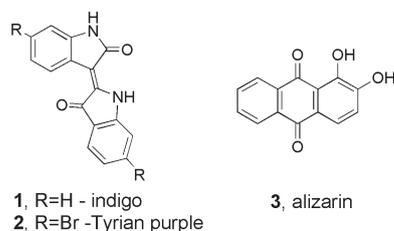
For thousands of years prior to this, dyers relied on dyes extracted from plants, insects and marine organisms. Painters had used variously coloured powders of metal-containing ores and minerals dispersed in 'drying' oils, such as the fatty acids extracted from the seeds of some plants or animals. With the profusion of artificial colourants so familiar to us today, we forget the ingenuity of our ancestors from many cultures who discovered how certain coloured natural substances could be fixed or bound to objects, to give a durable finish that resisted removal by water, *wash-fast*, or fading by exposure to light – *light-fast*.

The very first colourants used by man, perhaps ten or fifteen thousand years ago, were iron oxides, charcoal and chalk rubbed onto a surface or deposited as a suspension in water. As textile fibres and weaving developed, so the technology associated with dyeing grew in sophistication. It was discovered that cellulosic fibres obtained from

plants such as linen and cotton could be coloured to give a reasonably fast finish with *vat dyes*, such as indigo **1**, which is still used today in blue denim clothing, and Tyrian purple **2** extracted from molluscs (Chart 2). This famous purple dye was the most valuable commodity in the ancient world and was traded widely throughout the Near East and Europe; it generated the wealth that enabled the Phoenician Empire to flourish during the 2nd and 1st millennia BC. The first large industry producing a chemical was the extraction of the dibromoindigo dye from certain types of mollusc. It is estimated that 10,000 of these shellfish were required to produce just one gram of dye. Vast middens of crushed molluscs have been excavated at sites around the Mediterranean providing evidence of the existence of substantial purple dye-extraction operations. The chemistry underlying the use of these vat dyes is complex. It requires an initial reduction of the indigo (or thioindigo) molecule by anaerobic fermentation to a water soluble form and then after it has been applied to the textile aerial oxidation provides the insoluble form.

Another class of natural dye is the anthraquinones. The best known of these is madder, which comes from the root of the madder plant, and consists of a mixture of many closely related anthraquinones, the principal one being alizarin **3** (Chart 2).² Such molecules are water-soluble in their glycosidic form (with sugar groups attached) but, because of their flat molecular profile, they can intercalate cellulosic structures and be *locked* in place within the fibre by hydrogen bonding between the hydroxyl groups of the cellulose and those of the hydroxyquinone. Alizarin was first synthesised in Germany in 1868. To make the synthetic version of the dye water-soluble the molecule is sulfonated. Such dyes, when they are used without a metal ion mordant, are known as *substantive* or *direct* dyes. Traces of madder, applied as a direct dye, have been found on the linen cloth used to wrap Egyptian mummies including that of Tutankhamun, *ca.* 1350 BC.³

Chart 2. Some historic dyes



4, mordant-attached dye to cellulose fibre (schematic)

Cellulosic fibres from plants are very much more difficult to dye than the proteinaceous fibres of animals where metal ion mordants can be employed to fix the dye molecule to the fibres. These cationic mordants fix dyes by binding to the abundant anionic carboxylic acid groups, associated with the glutamic and aspartic acid residues present in proteins and simultaneously having ionizable polyphenolic and negatively charged dye ligands such as flavonoids and quinones attached as shown by **4** (see Chart 2). Anthraquinones can be used as direct dyes when used on cellulose but with the advent of white wool, they became almost exclusively used as metal ion mordant dyes because these gave more brilliant colours.

The liganded dye molecules form charge-transfer complexes with the metal ions and these absorb strongly in the visible region of the spectrum and therefore are highly coloured. The positions of their absorptions depend on redox potentials and hence on the nature of the metal ion. As a result, a number of different colours can be obtained from a given dye molecule by using different metal ions. The earliest and most commonly used metal ion was aluminium but iron, copper, tin, lead, and zinc were also used. Until fifty years ago, the British Army's scarlet or *red coat* tunics were dyed with a mordant dye formed between the cochineal anthraquinones (obtained from an insect) and tin ions. Thus, the first great revolution in dyeing and associated technologies was when, in the second half of the 1st millennium BC, the Romans succeeded in breeding sheep with white fleeces thereby providing a plentiful source of proteinaceous fibre for dyeing with mordant dyes. Prior to that, the Bronze and Iron Age sheep had dark wool that was unsatisfactory for dyeing because the colour did not show up against the dark background.

The chemistry of the natural dyes and pigments used by Maori prior to European contact, and the relationship between these colourants and those used by other cultures throughout the world to decorate their heritage objects follows.⁴ Problems with the stability of the colourants are discussed as well as treatments that have been employed to retard their degradation.

Maori Dyes

Prior to European contact, NZ had no hair or fur-bearing animals apart from the Polynesian dog, kuri. The Maori's principal textile fibre, harakeke, was obtained from the leaves of *Phormium tenax* (from Latin - strong basket) which is a cellulosic fibre with morphology very similar to that of linen – hence the common name for the plant of the New Zealand flax. The other main fibre used was from the *Cordyline* (cabbage tree) genus. These cellulosic fibres limited the classes of dye molecules that could be satisfactorily fixed to such fibres. Although many NZ plants contain compounds such as anthraquinones and flavonoids (from Latin *flavus* - yellow), these usually require a metal ion mordant and therefore are unsuitable for dyeing cellulosic *P. tenax*.

Indigo-bearing plants appear to be rare, if present at all in NZ, and so the only vat dye that could have been available would have been the purple dye from the indigenous mollusc. However, there does not appear to be any record of

its use by Maori. There were four colours of fibres used by Maori weavers;⁵ undyed, and three principal dyes: black - iron-tannate: yellow - Raurekau bark, and red/brown - Tanekaha bark.

Undyed fibres

There is a wide variation in the colour of the fibres extracted from *P. tenax* ranging from white to yellow/brown depending on the plant variety. Maori weavers prized the white fibres to enhance the contrast of the patterns in the garments they wove and it is probable that certain varieties were selected for this accordingly.

Work carried out in our laboratory has found that some varieties of *P. tenax* contain a number of substituted coumarins,⁶ a number of hydroxylated derivatives which emit strong blue fluorescence when excited with radiation in the near UV region of the spectrum; they have been used commercially as optical whiteners and brighteners.^{7,8} However, they are very photochemically active and have been shown to contribute to the photoyellowing and tendering of textile fibres to which they are applied.⁸ It has been established that reactive oxygen species such as hydrogen peroxide are produced by irradiation of wet wool containing these fluorescent whiteners.⁹ We have observed that a number of varieties of *P. tenax* exhibit fluorescence at 450 nm which is excited maximally at 340 nm. This emission is consistent with fluorescence originating from naturally occurring hydroxycoumarins. Further, irradiation of wet, undyed *P. tenax* fibres with UV radiation from 360-400 nm results in the formation of hydrogen peroxide and is accompanied by yellowing of the fibres.¹⁰

In unpublished work from our laboratory,¹⁰ it has been found that treatment of *P. tenax* fibres with alum (potassium aluminium sulfate) resulted in significant colour changes. Soaking in aqueous alum solution at ambient temperature created a yellow chromophore which reflectance spectroscopy showed to have an absorption maximum at 430 nm. There was also a featureless, but diminishing absorption extending to 600 nm. This is attributed to complexes formed between aluminium ions and polyphenolics in the fibre.¹¹ Subsequent rinsing of these fibres in hot water for 30 min at 90°C removed the coloured complexes and produced a very white fibre. The reflectance spectrum of the fibres treated in this way showed no detectable absorption in the visible region of the spectrum beyond ~400 nm. Apparently the aluminium complexes are soluble in hot water and extract the natural chromophores from the fibre. There are deposits of alunite, the hydrated potassium aluminium sulfate ore, in volcanic/geothermal areas of NZ, e.g. the Taupo volcanic zone, the *Alum Lake* and *Alum Cave* at Orakeikorako near Wairakei.¹² In this context it is interesting to note reports that a Maori chief from the Taupo region wore a startlingly white cloak woven from *P. tenax* fibres at the signing of the Treaty of Waitangi in 1840.¹³

Black dye

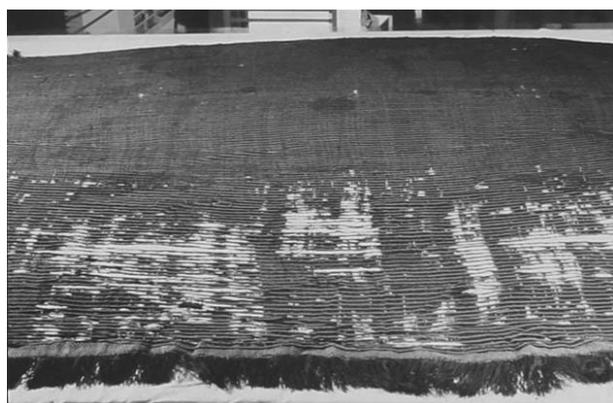
Black dye is a charge-transfer complex formed between iron(III) and catechol groups of tannins as shown by **5** (Chart 3). The tannins were obtained from the bark of cer-

tain trees; the gallotannins from hinau bark and the condensed tannins from a mixture of manuka and kanuka. The two types of tannin produce slightly different hues; the gallotannins give a deep bluish-black whereas the condensed tannins produce slightly less intense blacks and with a greenish hue.¹⁴

The method used by the Maori weavers for black dyeing was to soak the *P. tenax* fibres or muka (extracted from the leaf by scraping off the green epidermal layer) in an infusion of bark that had been simmered in water for several hours. The fibres were dried without rinsing and a coating of tannin is formed on the fibres. The fibres were then covered in a fine-textured mud, *paru* - which has a high iron content - for several hours. The excess mud was removed and the fibres, thoroughly rinsed with cold water to remove the remaining *paru*, were then exposed to sunlight to develop the black colour.⁵



Piu piu (waist garment) with degraded black fibres



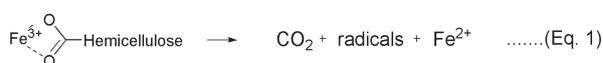
Loss of black dyed warp fibres in traditional Maori cloak

A number of cultures have independently discovered the same type of black dyestuff based upon an iron-tannin complex, although the source of iron and tannin differed depending on the local materials. The ancient Egyptians used it as ink on papyrus and linen. It was used extensively both as a dye and as ink on wool, cotton, linen, paper and parchment in Europe for many centuries; it was used to write Magna Carta. It was used as a dye in Mali, in Africa, in South America, and throughout Polynesia.

When it has been applied to textile fibres or paper, it slowly degrades the underlying substrate that eventually dis-

integrates. Not only is there a loss of mechanical strength and flexibility but the dye also fades. The chemistry of this degradation is not fully understood. Our research team and colleagues overseas have been studying the process in order to find ways of arresting it, or at least slowing it down. It has been established that the deterioration of the fibre involves water and oxygen, and it is accelerated by acid.¹⁵ As ageing and degradation proceed, the substrate evolves acetic acid and this further exacerbates degradation.¹⁶ It is interesting to note that when iron-tannate inks were used on parchment - animal skin that has been treated with lime - there is no noticeable degradation, e.g. Magna Carta. Presumably, acids produced during degradation are neutralized by lime residue in the parchment. Conservators at the British Museum, which has a large collection of black dyed woven *P. tenax* dating back to Captain Cook's visits to NZ, have been experimenting with weak alkaline reagents such as magnesium bicarbonate to neutralise the acid formed during ageing of the *P. tenax*.¹⁷

We have found that accelerated thermal ageing of black-dyed *P. tenax* results in the evolution of carbon dioxide that is linked to the degradation of the fibre. We believe that excess iron(III) in the dyed material is complexed (or bound) to carboxylic acid groups associated with the hemicellulose component of the fibre and that these decarboxylate with the formation of CO₂ and reactive free radicals (Eq 1). The radicals can cleave the cellulosic polymer backbone resulting in its fragmentation and a consequent loss of the mechanical integrity of the fibre.¹⁸



One strategy to avoid this degradative chemistry has been to give the fibres a second treatment with tannin after dyeing to scavenge the excess iron(III) that would otherwise bind to the carboxylic acid groups. This approach is very effective and slows the degradation of black-dyed fibres. Furthermore, it has the advantage that it does not involve the introduction of any materials that are foreign to the traditional dye process.¹⁸

In mediaeval times, the problem of the degradation of textile fibres by black iron - tannin dye was well recognized and prompted the Doge of Venice to ban its use to dye wool.¹⁹ However, it was later found that pretreatment of cloth with indigo provided some stabilization of the black-dyed fibres and a 1581 act of the English parliament required dyers to dye a *ground* of indigo on wool cloth before the application of iron tannate dye.²⁰ In Germany, as far back as the late 18th century, mention is made of an iron-tannate ink containing indigo, the blue dye.²¹ Stephens is credited with the invention of *blue-black* ink in 1832 and this contains an indigo additive; Stephens and Arnold started manufacture of this ink in the early 1830s.²² One benefit of including indigo was its stabilization of the ink. Like the catechol and gallo moieties of tannin, indigo forms a strong complex with iron(II) and -(III).²³ It removes iron ions bound to the carboxylates associated with the hemicellulose component of the paper fibres and, consequently the degradation that would otherwise result from decarboxylation. The English poet,

John Clare, wrote in 1832 that he had produced his own iron-tannate ink containing indigo and made his paper from birch bark.²⁴ Although this paper is very white, it has an extremely high content of a pectic acid, 4-*O*-methylglucuronoxylan, a characteristic of trees of the *Betula* family,²⁵ and is therefore subject to extensive hydrolytic deacetylation accompanied by the release of acetic acid that catalyses the degradation of the ink. Indeed, the smell of vinegar has been reported from Clare's manuscripts and the ink is badly degraded.²⁶ In this case the acetic acid appears to have negated the stabilizing activity of indigo.

A similar approach to preserving iron-tannate inks has been employed by present-day conservators at the Netherlands Institute for Cultural Heritage. They have used salts of phytic acid, polyphosphates, to complex and scavenge excess iron(III) that could otherwise initiate degradative decarboxylation reactions in the fibrous substrate.²⁷

Maori Golden Yellow Dye

When raw muka is placed in a boiling infusion of the bark stripped from raurekau (*Coprosma areolate*) for several hours, the fibres are dyed to a rich golden yellow. The dye molecules in raurekau belong to the anthraquinone family, as described above for madder. Although most anthraquinones are red at neutral pH, those present in raurekau give a more yellow hue. The principal anthraquinone in raurekau has been identified²⁸ as morindone **6** (Chart 3) the same compound found in the plant family *Morinda* of SE Asia. When applied to *P. tenax* in the way described above, it produces a very good wash and a light-fast finish.

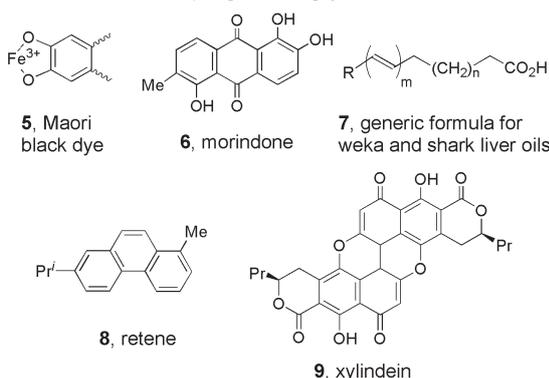
Red/Brown Dyes

Tanekaha (*Phyllocladus trichomanoides*) bark produces a tan colour. It is collected and treated in the same manner as that for hinau bark. Muka is soaked in the tannin solution for 12 hours whereupon the fibres are a rusty-brown colour. They are removed from the tannin solution, rubbed into warm wood ash (alkaline potassium compounds) while still moist and then exposed to sunlight for up to an hour before being thoroughly washed and left to dry.⁵

The bark of tanekaha is rich in a class of condensed tannin known as the proanthocyanidins. The development of colour with hot alkaline wood ash suggests that polyphenolics are being converted to the red anthocyanidin products widely found in plant material. This colour gradually fades in time to a pale tan, but the intensity and hue can be restored by further treatment with dilute alkali. The quinonoid oxidation products of phlobaphenes, familiar in the vegetable tanning of leather, are also believed to contribute to the red colour of this dyestuff.²⁹

Herries Beattie's ethnological records *Traditional Lifeways of the South Island Maori*³⁰ is an invaluable collection of description of technologies, methods and customs of pre-20th century Maori. As well as the dyes already discussed, he notes that a red dye that could be used as an ink was extracted from the kokihi plant. However, it could not be used as a textile dye because it was not wash-fast. Similarly the yellow flavonoid dyes obtained from puriri cannot be fixed to cellulosic fibres.

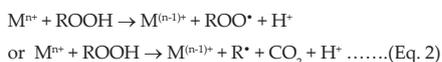
Chart 3. Some Maori dyes, paints and pigments



Paints and Pigments

A range of coloured paints was prepared from inorganic and organic pigments dispersed in a drying oil as a vehicle for their application. The vehicles used by Maori were shark liver oil or weka oil. These drying oils are polyunsaturated fatty acids of generic formula **7** (Chart 3) that polymerize to a solid by free radical chain reactions. These types of oils were, and still are, the basis of Western easel painting. The best known and oldest of these is linseed oil, extracted from the seed of the linen plant, and it was used by the ancient Egyptians. Other drying oils that have been used were from the poppyseed and the walnut.

The involvement of double bonds in the *drying* reaction means the rate of polymerization (or drying) depends on the number of double bonds present. Also, the presence of various metal ions and metal oxides, e.g. lead oxide in lead paints, causes decarboxylation of the fatty acids and the generation of free radicals, and they are therefore useful promoters of drying (Eq. 2). Conversely, some organic pigments contain aromatic residues that are free radical scavengers and terminate the polymerization thereby inhibiting solidification. Examples of such pigments are the sooty materials produced by burning the terpenes in resinous woods and gums. These dark/black pigments are a mixture of carbon (charcoal) with partially reduced and aromatized terpenes such as retene **8** (Chart 3). These dark pigments were much favoured in various schools of European easel painting for their lustrous and translucent finish, e.g. Rubens and Van Dyck,³¹ but because of their slow drying, small quantities of lead oxide were sometimes added to accelerate the polymerization of the oil vehicle.



The pigments and paints used by Maori before European contact were similar to those used by other cultures. Their black paint, like that just described in Europe, was made from soot collected on the leaves of harakeke from burning resinous woods such as rimu and mixing with shark liver oil or weka oil.³² This paint was used from the Archaic Maori period in rock art on the walls of limestone shelters in the South Island dating from as early as the 15th century. Maori painters also extensively used ferric oxide minerals to produce pigments with colours ranging from yellow ochre to red ochre. The yellow goethite is a hydroxy/hydrated ferric oxide and can be converted to the red haematite, Fe₂O₃ by roasting the yellow ore.³² Research in our laboratory is seeking to confirm textual and anecdotal

total reports of materials processing being practised by pre-European-contact Maori in the production of their red pigment from goethite. In some areas, where they were available, bluish clays – ferric phosphates – were also used as pigments.

An interesting organic blue pigment reported by Beattie³⁰ was obtained from decaying inner wood of the tawai. The dry dust, which is probably a tetrahydroxynaphthalene oligomer derived from a fungus growing on the wood, was moistened with water and then mixed with a drying oil. It was applied to fibres as a fluid suspension as for a dye, or thickened and used as paint.²⁹ A green colourant which is also derived from the NZ fungus *awheto*, *Cordyceps robertsii*, is that traditionally used in tattooing (moko).³⁴ Green fungal secondary metabolites are produced as intermediates in the fungal melanin biosynthetic pathway by polymerization of tetrahydroxynaphthalene. One of these green compounds has been identified as xylindein **9** (Chart 3) produced by fungi of the *Chlorosplenium* genus.³¹

Back to the Future

The emphasis of this paper has been the history of traditional dyes and pigments. There are intriguing parallels in the chemistries of the materials used by pre-European-contact Maori and the colourants used by other civilizations before the advent of synthetic dyes. From locally available raw materials peoples of different cultures independently discovered the same classes of chemicals and used them to decorate their textiles and other objects. However, it is instructive with present day concerns about environmental pollution, to reverse the perspective from the past to the future and close with a brief discussion about dye auxiliary agents.

Although it is fair comment that dyeing took a giant leap forward in the middle of the 19th century with the synthesis of dyestuffs, commercial dyeing has the rather tarnished image of the *dark satanic mills* of 200 years ago. For example, it was found that chromium was a particularly effective mordanting agent and it became, and still is, widely used in this capacity. However, it is very toxic and now its discharge is tightly controlled. Similarly, while chlorination of many fibres significantly improves the fixing of dyes to the fibres, the toxic organohalides produced are unacceptable; as is the discharge of unfixed dyestuffs into waterways. In our quest for a *green and pleasant land*, finding ways of cleaning up the dye process has become an industrial imperative. The global market for auxiliary agents that improves the fixing of dyes is ~\$NZ 3 billion p.a. and is growing at a rate of 6.5% p.a., driven largely by stringent environmental regulations and reducing energy costs. Without disclosing the details, there is a step used by Maori to produce the black dye that has the potential to be developed into an environmentally benign way of priming natural fibres for the more efficient uptake and fixing of commercial dyes.

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