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The Identification of Red Lake Pigment Dyestuffs and a Discussion of their Use

JO KIRBY AND RAYMOND WHITE

On 23 February 1815, a lecture was read at the Royal Society giving an account of the experiments performed by Sir Humphrey Davy on early Roman pigments from wall paintings and sites in Rome then being excavated. One pigment, in a broken vase found at the baths of Titus, was 'a pale rose colour; where it has been exposed to air, it has lost its tint, ... but the interior has a lustre approaching to that of carmine.'[1] The effects of mineral acids and alkalis on the pigment and its behaviour on combustion suggested that it might be a lake, although, as it did not compare very well with modern samples of cochineal and madder lakes, Davy wondered if it might be Tyrian purple. In a note he commented that the French chemist Jean Chaptal had decided that the pale rose-coloured lake from Pompeii that he had examined contained a dyestuff of vegetable origin, because of 'its not affording by decomposition the smell peculiar to animal substances'.[2]

Our knowledge of the chemistry of organic substances has grown immeasurably since the early nineteenth century and methods for the analysis of naturally occurring dyestuffs have acquired a level of sophistication unimaginable to Davy and Chaptal. Progress in analysis has been achieved largely in the field of textile dyes, however; precise identification of what may well be the same colorants in traditional lake pigments has proved a more intractable problem. It has been necessary to rely on the evidence of pigment recipes and other documentary sources for much of the information at present available.

If a survey is made of the recipes used for the preparation of lake pigments between about 1400 and 1890, the dyestuffs most frequently mentioned are those extracted from brazilwood, madder, and the scale insects, kermes, cochineal and lac.[3] On the aluminium-containing substrates widely used up to the nineteenth century at least, madder gives a more orange red than the others, while lac and cochineal can give quite blue-toned crimsons (Plate 1).[4] The recipes indicate that the overall pattern of dyestuff usage changes over time. Up to the early seventeenth century, the sources of dyestuff appear to be brazilwood, lac and shearings of cloth dyed with kermes (and perhaps the different species of cochineal): the '*cimatura de grana*' of fourteenth- and fifteenth-century Italian treatises.[5] The fact that madder is barely mentioned partly reflects the possibility that cloth shearings were also the source of this dyestuff; it may also reflect an accident of survival of the earlier written sources, or simply that those in the Flemish, Dutch or German dialects have so far been less thoroughly researched. It seems certain that there are strong links with the textile dyeing industry at this time. From the late sixteenth century onwards, the references to cochineal (the Central American species) become ever more frequent and the use of shearings appears to decrease. By the nineteenth century, the most important sources for artists' pigments appear to be cochineal and madder, lac and kermes being barely mentioned. The lack of durability of brazilwood dyestuff had long been known; it was not generally recommended for use as a high-quality artists' colour, although it was perfectly adequate for use in manuscripts, where it would receive relatively little light. The frequent mentions of brazilwood in earlier sources reflect the fact that many of these were written primarily for scribes and manuscript illuminators.

There are two principal difficulties in analysing a lake pigment dyestuff, the first of

Plate 1 Examples of dyed textiles and lake pigments. Foreground, left to right: kermes-dyed wool, kermes lake, brazilwood-dyed wool, brazilwood lake, madder-dyed wool, madder lake. Second row: lac lake, lac-dyed wool, cochineal-dyed wool (heavily dyed), cochineal lake. Painted glass plate (left to right): kermes, lac, cochineal and small sample of Polish cochineal, brazilwood and madder, all in linseed oil. At rear, silks dyed with kermes (dyed twice), cochineal (dyed once) and kermes (dyed once).

which is the small size of sample available. In a traditional lake pigment, the dyestuff is often present in quite low concentration. In a sample of the modern pigment alizarin crimson prepared in the laboratory, using a typical recipe, the amount of alizarin dyestuff used was approximately 30 per cent by weight of the final yield of pigment.[6] It is no surprise that the colour of alizarin crimson is very intense (Plate 2a). In contrast, the photomicrograph of a cross-section prepared from a sample of reddish-purplish paint from the robe of Saint Paul in *The Virgin and Child with Saints Peter and Paul* (NG 774), by Dieric Bouts, shows that a fifteenth-century madder lake is very much less intense in colour: the proportion of dyestuff in the lake, seen here mixed with the blue mineral pigment ultramarine, is very much lower (Plates 2b, 3). Admittedly not all early lakes contain a low concentration of dyestuff: some are extraordinarily intense in colour when examined under the microscope. A paint sample may consist of several layers of pigment bound in paint medium; only one of these may contain lake pigment. As traditional lake pigments are translucent they are frequently used as glazing pigments; applied over other paint even a thin glaze is very effective, indeed, as far as dyestuff content is concerned, perhaps deceptively so. The proportion of medium present in the glaze is usually quite high. This may be partly explained by a desire for transparency; also, in the case of lakes in an oil medium, a large proportion of oil is necessary to produce a workable paint, in other words, lake pigments have a high oil absorption. Thus even if the sample taken contains a high proportion of the glaze layer, very little lake pigment may be present.

The other principal impediment to dye identification has been the need to extract the colorant from the pigment for most analytical methods; in the case of a paint sample the pigment is bound up in the medium, rendering extraction difficult.

Methods of analysis

The methods generally used for the examination of dyestuffs can be divided into those based on electronic or vibrational spectrometry and those depending on chromatographic separation of the colorants into their individual components. The two may be combined, as in gas chromatography–mass spectrometry (GC–MS), for example, although the use of this particular technique for dyestuff analysis is not yet well developed. Chromatographic methods are the more precise and informative; certain spectrometric methods have the advantage that they may be used non-destructively on the object itself.

UV-visible absorption spectrophotometry, often used for dyestuffs in solution, can be used for pigment identification, but, using conventional equipment, is not an appropriate method for small samples from paintings.[7] Fluorescence spectrometry, which has been applied to the identification of naturally occurring dyestuffs in solutions of concentration 10^{-2} to 10^{-4}µg/ml,[8] has, however, been applied successfully to the examination of dyestuffs extracted from paint samples.[9] Spectrophotometric methods where reflectance or transmittance spectra of the dyed textile, pigment or paint are measured directly

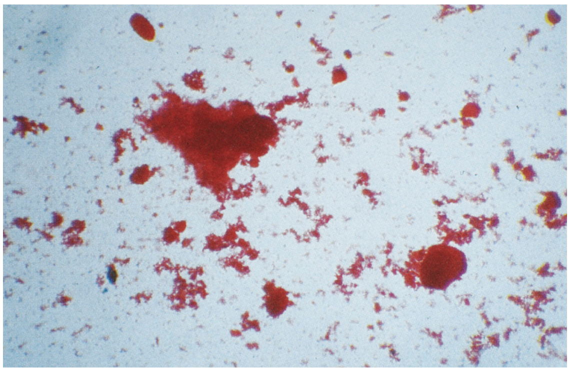

Plate 2a Roberson's alizarin crimson dispersed in immersion oil A. Original magnification 137.5 ×; actual magnification 110 ×.

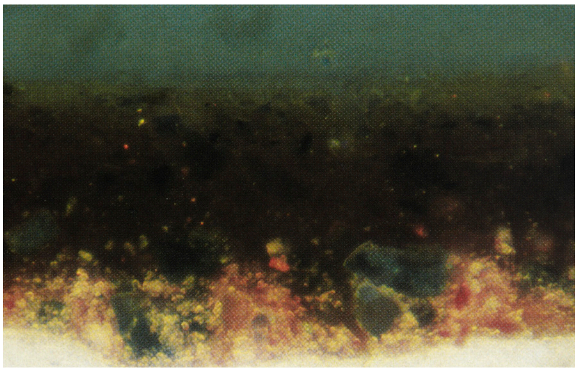

Plate 2b Dieric Bouts, *The Virgin and Child with Saints Peter and Paul* (NG 774). Cross-section prepared from a sample of reddish-purple paint from the robe of Saint Paul, showing a glaze of madder lake and ultramarine over a layer comprising madder lake, azurite and lead white. There appears to be a pale grey priming (lead white mixed with carbon black) below this. The lowest layer is the chalk ground. Original magnification 750 ×; actual magnification 590 ×.

Plates 2a and b photographed under the microscope by reflected light.

are less sensitive, although, compared with earlier instruments, microspectrophotometers now available give greatly improved reflectance curves over a broader spectrum.[10] The method developed in the National Gallery Scientific Department for the measurement of spectral transmittance curves of lake pigments in particles or thin cross-sections of paint is capable of greater sensitivity.[11] Reflectance microspectrophotometry can be used for non-destructive examination of materials, but the red colorants most frequently encountered up to the late nineteenth century are not reliably identified by this method: in an examination of dyed textiles, for example, accurate distinction between kermes and cochineal dyestuffs was not possible.[12] There is also the risk that mixtures of dyestuffs may be misinterpreted. Three-dimensional fluorescence spectrometry has been used as a non-destructive method of analysis on textile samples, but the instrumentation described is not suitable for paintings.[13]

Methods of analysis based on vibrational spectrometry have been less successful; although useful results have been obtained from naturally occurring colorants with an indigoid molecular structure, natural red dyestuffs do not come into this category. In practice the size of paint sample available for analysis has usually been too small for conventional infra-red spectrometry to be used. Fourier transform infra-red (FTIR) spectrometry, in which resolution is enhanced, is more powerful; when linked to an infra-red microscope the examination of small samples becomes possible. Since the use of FTIR was first proposed it has been applied to textile dyestuff analysis; it is rendered more complicated if the presence of bands from the mordant and the fibre must also be taken into account, as well as, perhaps, the effects of changes in the materials with time.[14] If a preliminary separation of the dyestuff components is carried out using thin-layer chromatography (TLC), FTIR may then be used for their identification.[15] Although spectra may be obtained from samples of lake pigment prepared in the laboratory, little success has been achieved with samples from paintings.[16] Raman resonance spectroscopy, coupled with a microscope, has been used with some success as a non-destructive method for the identification of inorganic pigments in manuscripts.[17] The identification of many natural organic dyestuffs is more difficult as the Raman signal is easily swamped by fluorescence from the dyestuffs themselves and from other organic materials present. While this can to some extent be filtered out by changing the excitation wavelength of the incident radiation, very few analyses of lake pigments or textiles containing natural dyestuffs have been reported.[18]

Thin-layer chromatography (TLC) has been used for extensive studies of red textile dyestuffs and, more recently, research on the constituents of naturally occurring and early synthetic textile colorants.[19] The method has also been applied to the analysis of lake pigments.[20] For several years a method derived from that developed using cellulose acetate plates was used at the National Gallery for the analysis of lake pigment dyestuffs; the substrate used was 85 per cent Polyamide 11, 15 per cent cellulose acetate (Macherey Nagel MN300 Ac-10), the plates being coated in the laboratory. This was found to give better separation and definition for hydroxyanthraquinone dyestuffs extracted from paint samples than cellulose acetate alone. The eluent used was chloroform/methanol/ ethyl methyl ketone/acetyl acetone in the proportions 8:10:5:1. In the late 1970s it became impossible to obtain the cellulose acetate powder and the method was discontinued in favour of high performance liquid chromatography.

In the last few years, high performance liquid chromatography (HPLC) has permitted quantitative identification of the constituents of colorants extracted from textiles and also from the source materials.[21] Such detailed study can assist in the taxonomic separation of closely related scale insect species; it has also enabled a more accurate distinction between, for example, the dyestuffs extracted from the Old and New World cochineal insects, the principal constituent of which is carminic acid in each case.[22] The research has been aided considerably by the use of a computerised diode-array detector, which permits detection at a wavelength range of 200–800nm and also allows the acquisition of a UV-visible absorption spectrum of a component during or after the analysis.[23] If the sample cell is to have an adequate window area for sufficient transmitted energy to fall on the detector, however, it must have a minimum internal volume of about 10μl. The amount of lake pigment dyestuff which can be extracted from a paint sample is usually so small that dilution to this cell volume weakens absorption to too great an extent; this has therefore limited the number of occasions when this method of detection of lake pigment dyestuffs has been possible.[24]

Plate 3 Dieric Bouts, *The Virgin and Child with Saints Peter and Paul* (NG 774), probably 1460s. Oak, 68.6 × 51.4 cm.

Experimental details

In order to use high performance liquid chromatography to examine lake pigment dyestuffs in paint samples, it has been necessary to accept certain limitations imposed by the small sample size and low dyestuff concentration. The use of microbore columns gives potentially higher chromatographic resolution and a considerable reduction in solvent volume, minimising dilution of separated components. The apparatus can easily be interfaced with the mass spectrometer, enabling further characterisation of the separated components. A disadvantage is that run times are very long. The choice of detector has been limited by the system chosen, which necessitates the use of a small detector cell volume, about 0.8μl, for good resolution at low flow rates of 10–20μl (one-hundredth of that for the conventional system). Until recently, the absorption cells in commercial diode-array detectors were too large to be used with a microbore system, although new developments in technology will help solve this problem. The disadvantage of the present system is that the detector and amplification system used appear to have about one-tenth of the sensitivity of more recent detectors, using carminic acid as a standard.[25]

Analysis is carried out on a modified system derived from Shimadzu LC-5A microbore HPLC modular components, adapted in this laboratory to provide gradient elution facilities. The apparatus consists of two LC-5A pumps under the control of a GRE-3A gradient controller, each connected by way of an SSI LP-21 damping unit to a Lee Visco Mixer (3µl hold-up volume). The eluent mixture is fed directly to a Rheodyne type 8125 injector fitted with a 2.5µl sample loop. Chromatographic separation is carried out using three 50cm Shimadzu ODS-18 reversed phase microbore columns connected in series. The effluent from the column is fed to a SPD-2AM variable wavelength UV spectrophotometric detector (range *c*.195–350nm), fitted with a 0.8µl internal volume flow cell, by way of an adjustable-split T-junction. The split ratio is set to about 4 to 1 in favour of the UV detector, the other line being connected to a VG Biotech Trio 2000 mass spectrometer, coupled by means of an electrospray/ionspray interface. The outlet from the flow cell is fitted with a SSI adjustable back pressure valve, set to about 3 atmospheres pressure (*c*.280kPa), to prevent bubble formation in the detector cell.

The solvent system has two components, (A) 94.9% water/0.1% trifluoroacetic acid/5% acetonitrile and (B) 95% methanol/5% acetonitrile, purged with helium before and during use. The presence of an acid in the eluent system was found necessary to suppress hydrogen ion formation, causing multiple, and tailing, chromatographic peaks. Originally acetic and formic acids were tried; these were replaced by *o*-phosphoric acid (2%) because of drifting retention times and poor peak shape, which deteriorated during the course of the run and was probably due to formation of esters with the methanol.[26] When examination of the colorants by electrospray-mass spectrometry commenced, it became apparent that molecular and fragment ionisation were suppressed and *o*-phosphoric acid was replaced by trifluoroacetic acid: at a concentration below 0.5%, minimal ion suppression is observed while chromatographic peak shape remains acceptable. The eluents are held at the starting concentration of 70%A : 30%B for 15 minutes; the concentration of B is then increased by 1%/minute to 45%, then by 0.5%/minute to the final concentration of 25%A : 75%B. The run is allowed to continue at this concentration for as long as necessary at a flow rate of 20µl/minute, the total run time being about six hours. The detection wavelength used for red dyestuffs is 275nm: not necessarily the optimum detection wavelength for every dyestuff component, but the most useful on average. It permits the detection of yellow dyestuff components which may also be present, although for these a detection wavelength of 255nm gives better results. The amplifier time constant is set to 2.5 seconds. Readings are at present logged on a Grant Squirrel recorder, type 1202, sampling at one reading a second; the range scale is set at 200mV (1mV being equivalent to 1×10^{-3}AU).

For the analysis of textile dyestuffs, the colorant is normally dissolved out using dilute hydrochloric or sulphuric acids mixed with an organic solvent such as methanol or ethyl acetate, followed by extraction into a suitable solvent.[27] Acid hydrolysis is not a satisfactory method for breaking up a highly polymerised paint film: transmethylation is more effective. The methylating agent boron trifluoride-methanol not only breaks up the paint medium,[28] but also, conveniently, dissolves the dyestuff out of the lake pigment. It has been found, however, that certain dyestuff constituents are altered to the extent that the colorant is no longer recognisable if the reagent is used at full strength and heated as in the standard procedure for methylation, kermes being particularly vulnerable; the commercially available reagent is therefore diluted to approximately 5 per cent. At this concentration partial methylation of the dyestuff components usually occurs, the degree depending on the quantity and strength of the reagent and for how long it remains in contact with the sample before analysis, as well as on the chemical structure of the components. It is advisable to test the strength of the reagent on a known pigment sample before use. 5µl ≈ 5% boron trifluoride-methanol are added to the sample which is then agitated in the ultrasonic bath and allowed to stand overnight; usually no further treatment is carried out, other than to centrifuge the sample before withdrawing a 2.5µl aliquot for injection onto the column.

The presence of the paint medium in the sample solution rarely causes more than minor inconvenience, unless it is very discoloured or present in great excess. It is possible to extract the medium from the paint, before examination of the dyestuff, using *m*-(trifluoromethyl) phenyltrimethylammonium hydroxide (TMTFTH).[29] The effect of the reagent on the dyestuffs is variable, but if the sample is left in contact with the reagent for as short a time as possible the dyestuff should be unaffected. Laboratory trials suggest that use of the reagent should be avoided with yellow lake pigments and if the paint is relatively recent (mid-nineteenth century or later). The residue from the treatment is washed very thoroughly with methanol to remove all traces of the reagent before addition of boron trifluoride-methanol, otherwise residual reagent produces a strong chromatographic peak in approximately the same region as alizarin. There is, of course, no reason why the residue should not be treated by acid hydrolysis as conventionally done; this will result in hydrolysis of the O–glycosides and probably certain other components eluted in this region of the chromatogram.

Results

The system was developed on a pragmatic basis to enable analysis of an important class of pigments about which frustratingly little was known, hindering study of the Gallery collection from a historical point of view, and from that of conservation. The intention has been to rectify this; primary research on the dyestuffs themselves has already been very well covered. The method used gives satisfactory and reproducible results under the conditions stated; background research into mechanistic aspects is necessarily of secondary importance and therefore proceeding at a slower pace.

Preliminary indications are that, under the conditions employed, partial methylation of carboxylic and possibly some activated phenolic functions takes place. This is illustrated in Figs. 1a and 1b. Fig. 1a shows the chromatogram of an aqueous extract of lac dyestuff from stick lac, the reddish or yellowish resin-like material secreted by *Kerria lacca* Kerr and other species, which forms an encrustation on the twigs of trees upon which the insects live, enveloping the insects themselves.[30] The dyestuff contains a mixture of laccaic acids, the principal constituents being laccaic acids A and B.[31] Fig. 1b shows the chromatogram of a sample of lac lake prepared in the laboratory, after treat-

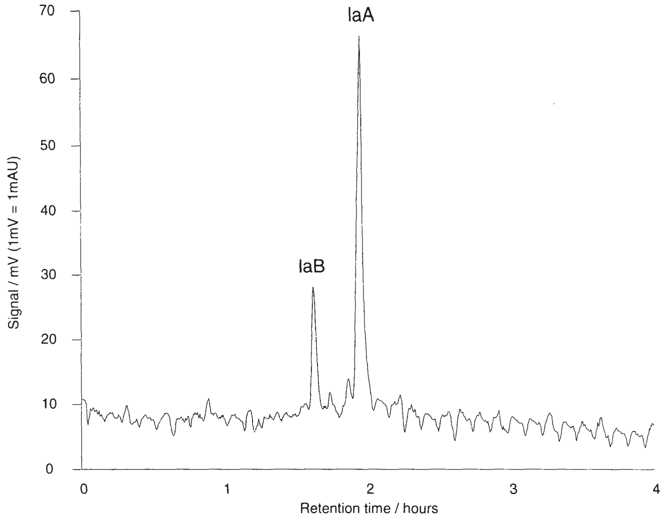

Fig. 1a Chromatogram of aqueous extract of lac dyestuff from stick lac (*Kerria* sp.); laA: laccaic acid A; laB: laccaic acid B. Eluents and conditions described in the text.

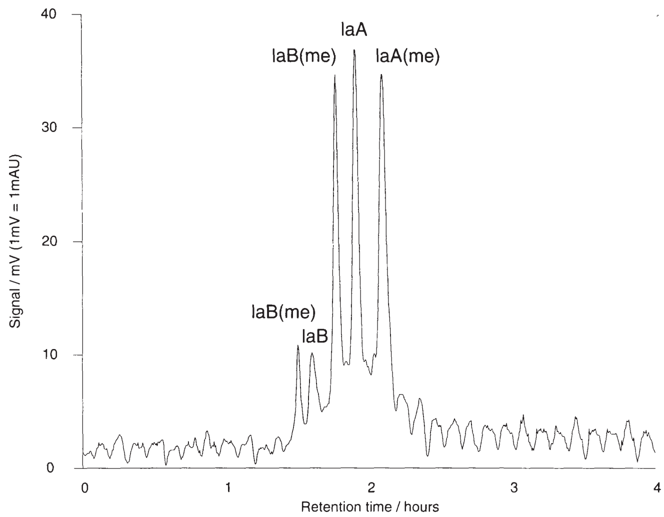

Fig. 1b Chromatogram of lac lake (prepared in the laboratory), after treatment with 5% boron trifluoride- methanol; laA, laB: laccaic acids A and B; laA(me), laB(me): methylated derivatives of laccaic acids A and B.

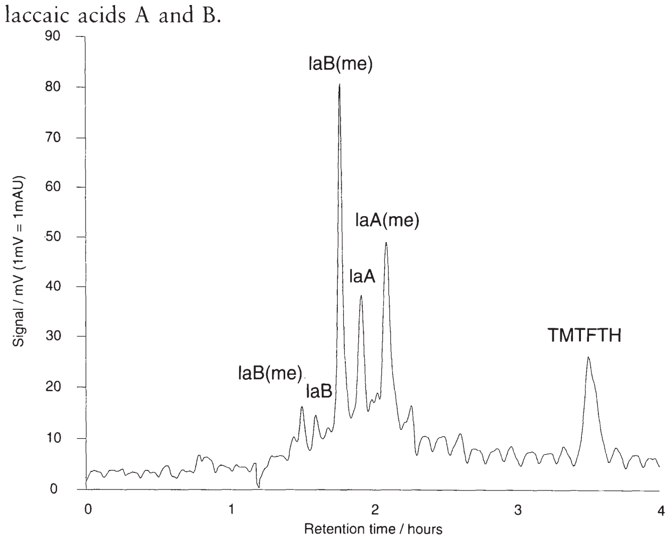

Fig. 1c Chromatogram of lac dyestuff extracted from sample of the red cloak, from *Cardinal Richelieu* (NG 1449), painted by Philippe de Champaigne, *c.*1637; after extraction of paint medium with TMTFTH, a trace of which has produced the peak thus labelled. Laccaic acids as before.

Plate 4 Philippe de Champaigne, *Cardinal Richelieu* (NG 1449), *c*.1637. Canvas, 259.7 × 177.8 cm.

ment with 5% boron trifluoride-methanol as described; the laccaic acid B complex tends to be methylated to a very much greater extent than laccaic acid A.

If the period of methylation is extended or the treatment is performed at a higher temperature, the proportion of derivatised components increases. If the reaction is pushed towards completion, which would be the normal practice, successful identification of the colorant is rendered more difficult. Fully derivatised laccaic and carminic acids are poorly resolved under these chromatographic conditions: unfortunately some compromise has had to be made with the eluent and gradient systems at present available and a ternary or quaternary gradient programming regime would undoubtedly be the ideal solution. Fully derivatised kermes dyestuff components are degraded; in earlier years, when more complete derivatisation was used with TLC as described above, occasional misidentification of kermes-containing lake pigments is known to have occurred. An example is the deep purple cloth of honour in Gerard David's *The Virgin and Child with Saints and a Donor* (NG 1432), painted in about 1510, which is painted in a red lake pigment mixed with azurite. Two analyses by TLC in 1978 indicated the presence of cochineal lake, apparently from the New World insect *Dactylopius coccus* Costa, a surprising result as it is unlikely that samples of the insects reached Spain before the 1520s or 30s and the earliest documented date for the import of the dyestuff into Europe is in the 1540s.[32] When another sample from the same robe was re-examined using HPLC (see Table 2, p. 72), carminic acid (the colouring matter of cochineal) was found to be present, but the principal dyestuff was that extracted from kermes, not identified previously because of degradation by the reagent. It is more likely that the lake pigment contains the dyestuff from an Old World insect, perhaps Polish cochineal, *Porphyrophora polonica* L., which contains a proportion of kermesic acid, mixed with kermes dyestuff.

Fig. 1c shows the chromatogram of lac dyestuff extracted from a sample of the dark red glaze of Cardinal Richelieu's cloak in Philippe de Champaigne's *Cardinal Richelieu* (NG 1449), painted in about 1637 (Plate 4). The principal laccaic acids and their methylated derivatives are clearly discernible. The sample had previously been treated with TMTFTH to extract the paint medium; the broad peak with a retention time of about 210 minutes is due to residual traces of this reagent.

While retention times generally remain consistent to about ±1–2%, they can be affected by changes in the ambient conditions, particularly temperature. It is therefore necessary to run standard samples for comparison (known pigments prepared in the laboratory, for example) or, preferably, to use an internal standard, measuring retention times relative to this.[33] To date, no entirely satisfactory internal standard for the system used has been found.

The principal component of the dyestuff extracted from brazilwood (*Caesalpinia* spp.) is the 4-arylchroman, brazilin, which forms brazilein on oxidation.[34] The main constituent of the freshly-extracted colorant is eluted at *c.* 88 minutes; treatment with the reagent causes degradation, giving a typical pattern of peaks at about 88, 97, 107 and 119 minutes. For comparison, the yellow flavonoid dye luteolin, found in weld and dyers' broom, is eluted at about 141 minutes.

The results obtained from paint samples are given in Table 2 (pp. 70–3). In several cases it has been possible to confirm and occasionally to amplify results obtained earlier by TLC. There is, however, a limit to what can be deduced from these chromatograms. Comparison of chromatograms given by paint samples containing a cochineal dyestuff and those given by standard solutions of carminic acid suggests that the amount of dyestuff present in the paint samples is usually about 1–2μg: 1 or 2 per cent of the weight of a paint sample about $0.5mm^2$ in size, containing other pigments and medium as well as the lake. Taking into account contributions from the paint medium (and perhaps from materials used in conservation treatments) to the chromatogram obtained and the limit of detection of the system in use, it is unrealistic to make any quantitative measures of individual dyestuff constituents or of their relative proportions when minor components must frequently fail to be detected. The published detailed studies of the dyestuff constituents have been based on extracts from the raw materials and dyed textiles; it has yet to be established how far the results of this research can be applied to the results obtained from lake pigment dyestuffs, particularly if these were extracted from textile waste: they may or may not be comparable. It should also be remembered that the amount of dyestuff available in the raw material and the proportions of its constituents will vary according to the time of year at which the material was harvested, the climatic and environmental conditions, and, in the case of lac for example, the host plant.[37] This is quite apart from the fact that the dyestuff constitution of plants often varies according to the part of the plant used and at different stages in the development of both scale insect and plant sources.[38]

In practice, this has had a bearing on the distinction between Old and New World cochineal insects, as well as on the further investigation of mixtures of dyestuffs such as kermes and madder, or kermes and cochineal. The principal dyestuff in cochineal insects is carminic acid. Polish cochineal, *Porphyrophora polonica* L. (Fig. 2),[39] which once occurred widely across Europe in Poland and other regions with light, sandy soils, also contains a variable proportion of flavokermesic and kermesic acids (the colouring matter found in kermes), equivalent to perhaps 6–9 per cent or more, depending on the method of processing.[40] Armenian or Ararat cochineal, *Porphyrophora hamelii* Brandt, which occurs principally in saline marshes in Armenia and Azerbaijan, contains very much less of these acids and without investigation of other minor components is hard to distinguish from the Central American insect *Dactylopius coccus* Costa.[41] If Polish cochineal dyestuff is present in low concentration (or if other organic constituents of the paint sample interfere) the small proportion of kermesic and flavokermesic acids may not be detected. Similarly, at these very low dyestuff concentrations, a mixture containing mainly the New World cochineal insect dyestuff with a small proportion extracted from kermes, *Kermes vermilio* Planchon, could be incorrectly identified. As a result it has not always been possible to state which cochineal insect was used; indeed, during the later sixteenth and early seventeenth centuries, when the Polish and New World insects were both available and in use in Western Europe, it would be perfectly possible to find a mixture of the two. By this time, however, the ready availability of the New World insect and frequent documentary references to it suggest that it was a more likely source of dye than the Armenian insect, in Western Europe at least.

Table 1
Typical retention times (in minutes) for some of the principal dyestuff constituents[35]

laccaic acid B	97
methylated laccaic acid B	91, 106
carminic acid	107
laccaic acid A	117
methylated laccaic acid A	126
methylated carminic acid	125
flavokermesic acid (laccaic acid D)	161
kermesic acid	172
alizarin	214
methylated flavokermesic acid	232
methylated kermesic acid	258
purpurin[36]	*c.*350

Discussion of results

Circumstances have dictated that a large proportion of the paintings examined date from the period between 1400 and 1600 and, within this group, rather more than half are assigned to Italian schools. In spite of this, a number of general points can be made.

If one considers the fifteenth and early part of the sixteenth centuries, and if it is also assumed that the paintings examined were fairly standard commissions, it can be seen that, broadly speaking, painters working in Italian city states and regions (Florence, Siena, Venice, Ferrara and other parts of Northern Italy) tended to use lake pigments prepared from scale insect dyestuffs, whereas those working in Northern Europe tended to use those prepared from madder, later with the addition of kermes. Relatively few results have so far been obtained from Northern European paintings and the pattern they form is less clear. Much later, during the seventeenth century, the use of the New World cochineal insect becomes widespread. This bears out the evidence suggested by the recipes. Brazilwood-containing lakes appear to have been little used; it is clear that brazilwood was not thought to be as good quality as other dyestuffs and probably its absence is partly explained by this.[42] It has also been suggested, on the basis of results from the analysis of textile dyestuffs, that brazilwood may have been unavailable in Europe from about the time of the fall of Constantinople in 1453 – which may have disrupted the supply of sappan wood, *Caesalpinia sappan* L., from the East – until the discovery of the New World species *C. brasiliensis* L. (brazilwood), *C. crista* L. (fernambuco wood) and *C. echinata* Lam (peachwood).[43] The poor permanence of the colour from these woods, which were imported into Europe soon after 1500, soon became apparent. In 1553, William Cholmeley described brazilwood as 'disceytfull' and 'a fauls colour' and his was a common complaint;[44] it would be interesting to know if they were any more or less 'disceytfull' than sappan wood in this respect.

Very much more is known about the use of the same dyestuffs on textiles over the same period. In Italy, kermes, Polish cochineal and, later, New World cochineal were used to a greater extent for high quality textile dyeing

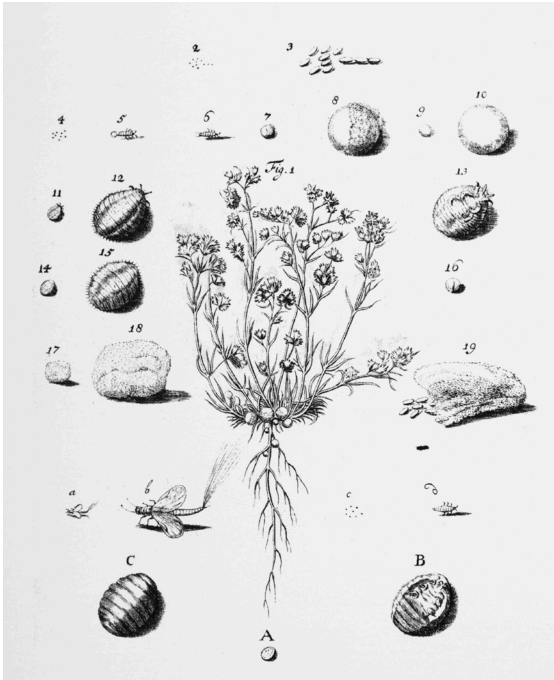

Fig. 2 Stages in the life cycle of Polish cochineal, here seen as cysts on the roots of the perennial knawel; the adult insect, drawings 11–15, is compared with the adult Mexican cochineal insect, drawings A–C. From J.P. Breynius, *Historia naturalis cocci tinctorii, quod polonicum vulgo audit*, 1731.[39]
By permission of The British Library.

Plate 5 Altobello Melone, *Christ carrying the Cross* (NG 6546), *c*.1520–5. Poplar, 49 × 63.5 cm.

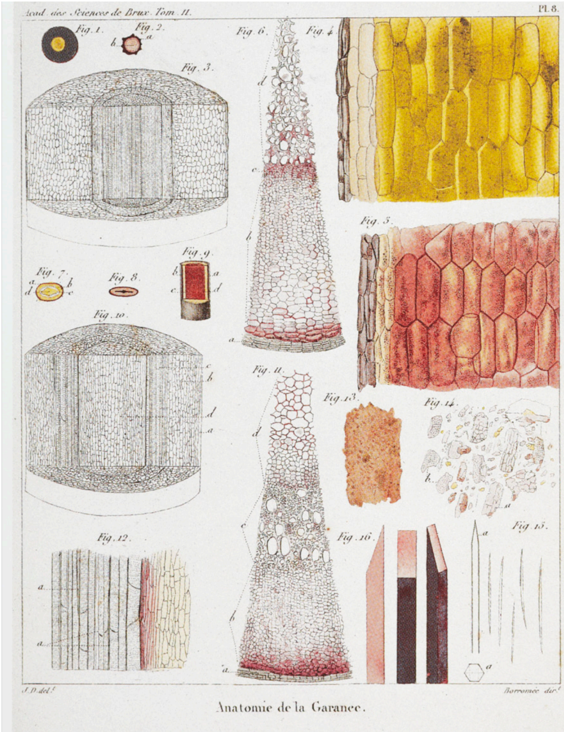

Plate 6 Structure of the madder root, in transverse and longitudinal section, at different stages in its development. Diagrams 4 and 5 illustrate the change in colour of the cut surface of the root from yellow to red on exposure to the air. Diagram 16 shows crystals of alizarin; for their colour, Decaisne used those obtained by Robiquet who, with Colin, was responsible for the isolation of alizarin and purpurin from madder in 1826. From J. Decaisne, 'Recherches anatomiques et physiologiques sur la garance', 1837.[50]
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than brazilwood or madder; lac was rarely used. In Northern Europe – Flanders, the Netherlands and Germany – madder was the most important dyestuff in the fifteenth and sixteenth centuries, kermes and the other scale insects being apparently little used before the sixteenth century. The use of New World cochineal grew in importance during the later sixteenth and seventeenth centuries.[45] However, guild statutes and records of duties payable for the movement of goods indicate that madder was available in Italy by the thirteenth century, but, like brazilwood, it was probably considered appropriate for different uses, then and later.[46] A closer study of both the results of analysis and dyeing recipes indicates that before the mid-sixteenth century, for example, madder was used to dye wool and silk in Venice and other Italian cities (but not what one would imagine to be the most expensive fabrics) while, shortly afterwards, cochineal was similarly used in Antwerp.[47] A greater range of goods, including dyestuffs, would be available around major international trading centres like Antwerp and Venice.[48] Perhaps on this account it is interesting that the single sixteenth-century example of madder lake identified so far in an Italian painting occurs in a work by a North Italian artist: *Christ carrying the Cross* (NG 6546), painted in the early 1520s by the Cremonese painter Altobello Melone (Plate 5; Table 2, p. 71). Similarly, kermes has been identified on sixteenth-century tapestries from Antwerp and Brussels, while kermes-containing lakes have been found in paintings by Gerard David, who worked in Bruges and Antwerp around 1484–1523, Ambrosius Benson, who worked in Bruges around 1518–50 (Table 2, p. 72), and in a group of altarpieces painted in Antwerp between 1495–1560.[49]

Over a long period the Netherlands, notably Zeeland and especially the region around Schouwen, were celebrated for the quality of the madder produced, while Southern France, Spain and other areas around the Mediterranean were the source of kermes. In madder, *Rubia tinctorum* L., and related species, the dyestuff constituents are found predominantly in the root, largely in the form of glycosides. The principal anthraquinones, alizarin and pseudopurpurin, occur largely as primverosides, the yellow colour of which can be seen if the root is broken; the colour of the broken surface gradually changes to red as the anthraquinones (which taste unpleasant and presumably have a protective function for the plant) are released (Plate 6).[50] The dyestuff is found under the bark of the root and through the central part; this portion, without the bark and outer matter, was the best, the so-called *krap* madder, and was the final product of pounding in the madder mill. The first product, *mull*, containing the most dirt, outer materials and tiny roots, was the worst (in eighteenth-century France it was known as *billon* and discarded); there were also other grades.[51] The grades, and the amount of dirt each was permitted to contain, were already fixed in the fifteenth century, as the Reymerswaal regulations for the production of madder of 1480 make clear.[52] The number of references to madder and its production in official documents in the Netherlands from the fourteenth century onwards indicate that the dyestuff was the centre of a highly developed industry.[53]

Although there are several species of *Kermes*, only one, *Kermes vermilio* Planchon, which occurs on the kermes oak *Quercus coccifera* L. (Fig. 3),[54] is of importance for its dyestuff. Another insect, *K. ballotae* Signoret, an albino form of *K. vermilio* Planchon, may occur on the same host tree. The dyestuff extracted from this insect contains about 80 per cent of yellowish flavokermesic acid, with only about 20 per cent of kermesic acid, the principal constituent of the *K. vermilio* dyestuff; the presence of significant quantities of this insect in the dyebath would thus adversely affect the final colour.[55] Italian sources of the fourteenth to sixteenth centuries refer to kermes (and apparently Old World cochineals, depending on the date of the source) under the name of *grana*. The Florentine merchant Francesco Balducci Pegolotti, in his merchants' handbook written around 1339–40, lists seven different types, including *grana di Schiavonia*, while the late fourteenth- or early fifteenth-century manual of the Florentine Arte della Seta, mentions *grana di cintri*, *Spagnuola*, *le barbaresche*, *la Valenza* and *la Provenza*.[56] One list given by the Venetian Gioanventura Rosetti in his *Plictho* of 1548 is very similar, while in an earlier chapter he lists fewer varieties, including *grana di Armenia*.[57] This last could be Armenian cochineal, but in many other cases the names probably refer to the same species of insect gathered in different localities, varying in dyeing quality. The Arte della Seta document also lists two types of *chermisi*, *chermisi minuto* and *chermisi grosso*, while seven types of *cremesino* are listed in the *Plictho*. *Chermisi minuto*, at one florin a pound, was twice the price of *chermisi grosso* and the most expensive variety of *grana*, *grana di cintri*; the silks dyed with these insects were also dearer.[58] The carminic acid-containing insects, the Old and New World cochineals, give a bluer crimson or pink (depending on the depth of dyeing) than kermes (see Plate 1, p. 57) and it is possible that the term *chermisi* refers to varieties of these insects – perhaps even to different species, although not, at this date, to the Mexican insect.[59] The laborious harvesting of Polish cochineal, which occurs on the roots of its host plant, usually the perennial knawel, *Scleranthus perennis* L. (Fig. 2), and the small size of the insect would undoubtedly contribute towards its expense as a source of colorant.

Fig. 3 *Ilex cocciglandiffera c.d.pin*: engraving showing kermes on its host, the kermes oak, from P.J. Garidel, *Histoire des plantes qui naissent aux environs d'Aix et des plusieurs autres endroits de la Provence*, 1715.[54] By permission of The British Library.

It is thus not surprising that scale insects and other dyestuffs were important items of trade; care was needed to choose good quality material. Pegolotti described how to examine *grana* by its weight and appearance and by chewing a sample; stick lac, *lacca*, both *matura* and *acerba*, is described in detail. He devoted almost as much attention to brazilwood and madder.[60] It is therefore understandable that shearings or clippings from expensive dyed textiles were re-used as a source of dyestuff, not only for pigments, but also in dyeing: the '*vlocken*' or '*bourre*' described in Northern European and French sources.[61] Lake pigment recipes describe how alkali was used to dissolve the dyestuff out of the textile waste; alum was then added to the coloured solution to precipitate the pigment. In fifteenth- or sixteenth-century recipes from the Netherlands and Germany, it appears that the alkali used was sufficiently strong to reduce the shearings to an amorphous, even gelatinous, consistency; it was deemed strong enough if it dissolved a feather.[62] Seventeenth-century descriptions of *bourre* in use seem rather similar.[63] In this case, the final pigment would contain much textile matter, not necessarily in a visually recognisable form. That this was not always so is evident from Italian recipes; in a typical example, from the fifteenth-century Bolognese manuscript, the alkaline dyestuff solution is pressed out of the textile fibres and the alkali is poured through again to extract more dyestuff. Clearly in this case the alkali used was less strong; a large part of the textile would remain in the filter.[64]

In a recent examination of Titian's *Venus and Adonis*, of about 1560, in the J. Paul Getty Museum, Malibu, microscopic examination of a cross-section prepared from a sample of the red glaze of the cloth draped over Venus' seat revealed the presence of a few textile fibres within the lake pigment, which contained both cochineal and madder dyestuffs.[65] While there are other possible explanations for the presence of the fibres (including the use of a piece of fabric to apply the paint or to level its surface),[66] the use of shearings in the preparation of the pigment is the most likely.

Plainly the precise dyestuff composition of a pigment so prepared would depend on that of the original textile matter, and thus also on that of the dyebath (or baths), its age, how many times it had been used and so forth. While it is not yet possible to throw much light on these factors, a clear connection between the preparation of lake pigments and textile dyeing may be demonstrated by the presence of a mixture of dyestuffs in a single pigment; there are, of course, several possible explanations for the presence of a mixture of dyestuffs in a sample of paint. It is quite common to find more than one layer of paint containing lake pigment and the lakes need not be the same. Yellow lake pigments may well occur unrecognised, mixed with other pigments, in layers of underpaint, quite apart from any possible admixture of yellow dyestuff with red dyestuff in a single lake pigment. This was found to be the case with several samples from paintings by Tintoretto in the Scuola di San Rocco, dating from the 1560s to the 1580s; the red dyestuff used was cochineal (probably the New World insect in most cases), but the complexity of the paint structure has made the interpretation of the presence of the yellow dyestuff difficult.[67]

Artists sometimes mixed two lake pigments together to obtain the desired colour; this has been observed in a number of samples from seventeenth-century paintings, including several by Rembrandt, where a cochineal-containing red lake was mixed with a yellow lake to give a more orange red.[68] Thus, although mixtures of cochineal with yellow dyes, such as turmeric, were used in dyeing in Holland at this time,[69] the presence of a similar mixture in a paint sample does not necessarily indicate the use of shearings of textile dyed thus to prepare the lake pigment: turmeric is occasionally mentioned in cochineal lake recipes not employing shearings. Pigment recipes suggest also that, by this time, the links between pigment and textile were gradually becoming less close. Examination of the paint sample under the microscope could not reveal whether the mixture of dyestuffs (cochineal, probably, and madder) present in the thinly painted red glaze of Pax's drapery in Peter Paul Rubens's *Minerva protects Pax from Mars ('Peace and War')* (NG 46), painted in about 1629–30 (Table 2, p. 73), was due to the use of two lake pigments, mixed by the artist, or not. The fact that the picture was painted while the artist was in England is probably not significant (both dyestuffs were used in England at this time);[70] it is interesting, however, that the English artist William Larkin (died 1619) used a mixture of madder and cochineal lakes for certain passages in his *Portrait of Susan Villiers, Countess of Denbigh* (private collection), painted between 1610 and 1619. In other areas, cochineal lake was used alone.[71]

In several of the paintings examined, there is no indication that two lakes have been mixed; the dyestuffs are present in one pigment. Madder and kermes, for example, occur together in the pigment used for the robe of a courtier in *Saint Giles and the Hind* (NG 1419), painted by the Master of Saint Giles, probably in Paris in about 1500; kermes and a variety of cochineal are found together in Lorenzo Lotto's *Portrait of Giovanni della Volta and his Family(?)* (NG 1047; Plate 7) of about 1547 (Table 2, p. 71). The presence of a similar mixture in the lake used for the cloth of honour in David's *The Virgin and Child with Saints and a Donor* (NG 1432) has been discussed above. The use of textile shearings as a source for the dyestuff is the most likely explanation for such mixtures. Similar results were obtained from the group of sixteenth-century altarpieces from Antwerp mentioned above, where not only kermes mixed with madder, but also kermes mixed with redwood (brazilwood), were found.[72] Brazilwood was sometimes used in textile dyeing to modify the colour given by madder or kermes, sometimes in imitation of the colour given by a better quality dyestuff.[73] In the one occurrence identified (Table 2, p. 72), it occurs mixed with madder in the faded pink dress of the Virgin in *The Virgin and Child in a Landscape* (NG 713), an early sixteenth-century painting attributed to Jan Provoost. In practice one cannot be sure that a pigment containing a mixture of dyestuffs can be related directly to a single textile dyed with this mixture: shearings from more than one textile could have been used. However, mixtures of kermes and madder were widely used in, for example, the '*meza grana*' dyeings described by Rosetti and the '*demy-graines*' or '*demy-cramoisis*' of seventeenth-century France;[74] if the shearings were from one textile, the original dyeing could have been of this type. In many recipes for dyeing with scale insects, a proportion of better-quality insect matter ('*pococco*' or '*poppo*') is introduced into the bath, perhaps as a 'starting' material; there was plenty of opportunity for mixing of insects to occur as more dyestuff was added as necessary and the bath was re-used until exhausted.[75]

There are few references to the use of lac dyestuff in textile dyeing in the fifteenth and sixteenth centuries; the results of analysis show that as a lake pigment it occurred widely over a long period. Pegolotti and others describe stick lac's tubular form, colour and grainy appearance very fully, while being unaware of its animal origins;[76] the 'large ants' that 'deposit the lacre' were first described to a European audience in 1563 by the Portuguese physician Garcia da Orta.[77] By the latter part of the seventeenth century the raw material was imported into Europe in large quantity by the English and the Dutch, but as much for the resin-like component which is the source of shellac as for the dyestuff. By the end of the eighteenth century, the crudely separated dyestuff was imported into England from India in the form of cakes of 'lac lake', of very variable composition, according to Edward Bancroft. His detailed account tells nothing of its use in Europe in the fifteenth century and earlier, however: he and other contemporary writers seem to have been largely unaware of this.[78] Too few results have been obtained from paintings dating from the mid-sixteenth century onwards to throw light on the later history of the use of the pigment in easel painting; one cannot say if the use of lac lake by Philippe de Champaigne in his portrait of Cardinal Richelieu (Plate 4) represents a relatively late occurrence or not. Certainly, fifty years later, French lake pigment recipes concentrate on cochineal – notably cochineal carmine – and brazilwood; Pierre Mignard used a cochineal lake in his painting *The Marquise de Seignelay and Two of her Children* (NG 2967) of 1691 (Table 2, p. 73).[79]

It appears that lac lake was the 'standard' lake used for easel painting in the fifteenth century in Florence, and probably other parts of Italy as well. Examples of its use are seen in paintings by four Florentine painters, Filippino Lippi, Domenico and David Ghirlandaio and Michelangelo (NG 1412, 3937, 2502 and 809), the subject in each case being a variant of the Virgin and Child theme, illustrated in Plates 3, 5, 6 and 7, on pp. 22–3 of this *Bulletin*.[80] In Filippino Lippi's painting, lac lake was used for the glaze on Saint John's cloak; in the paintings by Domenico Ghirlandaio and Michelangelo it was used for the dress of the Virgin, traces of kermes lake also being present. In David Ghirlandaio's painting lac lake was used to glaze red areas of the carpet, while the Virgin's dress was painted with kermes lake mixed with a little lac lake. Italian documentary sources of the fifteenth and sixteenth centuries generally refer to *lacca* and *lacca di cimatura*. Paolo Bensi, in an article on the Florentine Confraternità dei Gesuati of the Convent of San Giusto alle Mura, who supplied good quality pigments to painters during the second half of the fifteenth century, has suggested that the former referred to lac lake, while the latter referred to a lake prepared from shearings of cloth dyed, probably, with kermes.[81] The results of analysis obtained so far suggest that this is likely to be the case. Examination of the accounts of the Florentine painter Neri di Bicci indicate that, while *lacca* was expensive at 14 *soldi* an ounce in about 1466–71 (compared with 3 *soldi* for an ounce of the yellow lake pigment *arzica* and 4 *soldi* a pound for lead white), *lacca di cimatura* was perhaps about twice that price; only ultramarine and good quality azurite were dearer.[82] This was still the case nearly a century later in Venice: Lorenzo Lotto, who used what was probably a lake prepared from shearings in the *Portrait of Giovanni della Volta and his Family(?)* (NG 1047; Plate 7), paid 2 *lire* 15 *soldi* for an ounce of *lacca di grana* in 1542, but only 4 *soldi* for a pound of lead white.[83] In easel painting cost thus played a part in which pigment was used; in manuscript illumination this would be a less important factor, as the identification of a Polish cochineal lake – perhaps prohibitively expensive for use in most easel paintings – in a fifteenth-century Sienese manuscript suggests.[84] The presence of traces of one lake mixed with the other (most notably in the Virgin's dress in David Ghirlandaio's painting) could be explained by a desire not to waste expensive pigment, as much as for any reason of colour.

With the arrival of the dyestuff-rich New World cochineal insect in Europe, the use of kermes as a source of dye declined. By the mid-eighteenth century it was used for dyeing in Venice, according to Jean Hellot, while in France it was barely used at all; by the late nineteenth century the quantity used in Europe was negligible.[85] It remained available, however; like several of the materials used as sources of dyestuff, it had medicinal value. It has astringent properties and was also used to prepare a cordial (and subsequently a syrup) derived from the famous *Confectio Alkermes*, devised in the ninth century by the Arabic physician Mesue. This panacea was popular even into the nineteenth century.[86]

If kermes was used for dyeing, even on a small scale, there is no reason why the preparation of kermes lakes should not also have continued here and there. Recipes for kermes lake appear in some early nineteenth-century sources and George Field was given samples of French kermes lakes, although at the time he doubted their authenticity.[87] Kermes was identified in the lake pigment used for the Virgin's red dress in Boltraffio's *Virgin and Child* (NG 728), painted in Milan probably around 1493–9. The dress is one area of the painting known to have been repainted completely, probably before it left Italy in 1854;[88] this is thus a very late occurrence of a pigment which must have become difficult to obtain outside areas (such as Venice or Montpellier) where kermes still had some specialist uses. During the first thirty years or so of the nineteenth century, the improvement in methods of extracting madder dyestuff, following the work of Colin and Robiquet in France and Field and others in England, had resulted in greatly improved madder pigments; these, with cochineal pigments, became the artists' colours of choice until the final years of the century.

Plate 7 Lorenzo Lotto, *Portrait of Giovanni della Volta and his Family (?)* (NG 1047), probably 1547. Canvas, 114.9 × 139.7 cm.

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Table 2 Lake Pigment Dyestuffs

Artist	Title of Painting	Date	Sample	Dyestuff
ITALIAN SCHOOLS				
Lorenzo Monaco	*Adoring Saints* NG 216	probably 1407–9	Red robe of saint on left holding book, left-hand edge	Probably kermes[89]
Fra Angelico, Follower	*The Annunciation* NG 1406	*c.*1434	Crimson shadow of fold in angel's robe	Kermes
			Crimson glaze of roundel decoration on Virgin's dress	Kermes (possibly + lac)
Paolo Uccello	*The Battle of San Romano* NG 583	probably *c.*1450–60	Wine-red plume of helmet of foreground figure	Probably lac
Giovanni di Paolo	*Saints Fabian and Sebastian* NG 3402	*c.*1475–82	Saint Fabian's red robe	Kermes, probably + a little lac[90]
Filippino Lippi	*The Virgin and Child with Saint John* NG 1412	*c.*1475–80	Red of Saint John's cloak	Lac
Domenico Ghirlandaio	*The Virgin and Child* NG 3937	probably *c.*1480–90	Mid-pink glaze of Virgin's dress	Probably lac (possibly + kermes)
David Ghirlandaio	*The Virgin and Child with Saint John* NG 2502	probably *c.*1480–90	Red glaze of carpet	Lac
			Red glaze of Virgin's dress	Kermes (possibly + lac)
Filippino Lippi, Follower	*The Worship of the Egyptian Bull God, Apis* NG 4905	*c.*1500	Brownish-red robe of man on left with blue headdress, shadow of fold	Probably kermes[91]
Carlo Crivelli	*The Immaculate Conception* NG 906	1492	Mauvish glaze of cloth of honour	Probably kermes
Michelangelo	*The Virgin and Child with Saint John and Angels ('The Manchester Madonna')* NG 809	*c.*1497	Crimson shadow of fold in Virgin's dress	Principally lac
Francesco Bissolo	*The Virgin and Child with Saints Michael and Veronica and Two Donors* NG 3083	probably 1500–25	Red of Saint Veronica's dress	Kermes
Francesco Zaganelli	*The Baptism of Christ* NG 3892.1	1514	Saint John the Baptist's red drapery, shadow of fold	Kermes
Bacchiacca	*Joseph pardons his Brothers* NG 1219	probably 1515	Deep crimson of coat lining of figure with straw hat, left foreground	Kermes

Artist	Title of Painting	Date	Sample	Dyestuff
Altobello Melone	*The Walk to Emmaus* NG 753	*c.*1516–20	Red of Christ's robe	Kermes
	Christ carrying the Cross NG 6546	*c.*1520–5	Red of Christ's robe	Madder
Garofalo	*The Holy Family with Saints John the Baptist, Elizabeth, Zacharias and (?)Francis* NG 170	*c.*1520	Shadow in fold of Virgin's red dress	Lac
Vincenzo Catena	*Portrait of the Doge, Andrea Gritti* NG 5751	probably 1523–31	Red glaze on cap	Kermes
			Pink of sitter's right sleeve	Kermes
Lorenzo Lotto	*Portrait of Giovanni della Volta and his Family (?)* NG 1047	probably 1547	Deep red shadow in fold of woman's skirt	Kermes + trace of cochineal
Paolo Veronese	*The Consecration of Saint Nicholas* NG 26	1561–2	Red collar of figure in white cassock	Cochineal, probably Polish cochineal[92]
	Allegory of Love, I ('Unfaithfulness') NG 1318	probably 1570s	Deepest red shadow of tunic of man, left	Cochineal, probably the New World insect[93]
			Mid-tone of red drapery of man, left	Cochineal, probably the New World insect
			Reddish-brown shadow on orange tunic of man, right	Cochineal, probably the New World insect
	Allegory of Love, IV ('Happy Union') NG 1326	probably 1570s	Red of brocade dress, shadow, bottom edge	Cochineal, probably the New World insect
	The Adoration of the Kings NG 268	1573	Shadow of red drapery of kneeling king	Cochineal, probably Polish cochineal
Tintoretto	*The Origin of the Milky Way* NG 1313	probably 1575–80	Red drapery upon which Venus is seated	Lac[94]
Palma Giovane	*Mars and Venus* NG 1866	probably 1585–90	Shadow of red curtain, upper left corner	Cochineal (source unclear)
Neapolitan School	*The Adoration of the Shepherds* NG 232	probably 1630s	Red of Virgin's dress	Cochineal (New World)[95]
After **Guido Reni**	*Perseus and Andromeda* NG 87	1635–1700	Red drapery near Andromeda's hip	Cochineal[96]
Giovanni Antonio Pellegrini	*Rebecca at the Well* NG 6332	1708–13	Servant's red cloak, from lower left corner	Cochineal (New World)
Canaletto	*A Regatta on the Grand Canal* NG 4454	*c.*1740	Red of textile	Cochineal (New World)
SPANISH SCHOOL				
Diego Velázquez	*Portrait of Archbishop Fernando de Valdés* NG 6380	1640–5	Red glaze of curtain	Cochineal (probably New World)

Artist	Title of Painting	Date	Sample	Dyestuff
EARLY NETHERLANDISH SCHOOLS				
Rogier van der Weyden and Workshop	*The Exhumation of Saint Hubert* NG 783	*c.*1440	Red robe of figure on extreme left	Probably madder
Dieric Bouts	*The Virgin and Child with Saints Peter and Paul* NG 774	probably 1460s	Reddish-purple of Saint Paul's robe	Madder
Dieric Bouts, Workshop	*Christ crowned with Thorns* NG 712	probably 1475–1500	Red of Christ's robe	Madder
Netherlandish School	*The Virgin and Child with Saints and Angels in a Garden* NG 1085 Central Panel: *Mystic Marriage of Saint Catherine*	*c.*1500	Red glaze of fold of dress of woman, right	Probably kermes[97]
Master of Saint Giles	*Saint Giles and the Hind* NG 1419	*c.*1500	Red of courtier's robe, left-hand edge	Madder + kermes[98]
After **Quinten Massys**	*Christ* NG 295.1	probably *c.*1500–50	Wine-red of Christ's sleeve	Madder
Attributed to **Jan Provoost**	*The Virgin and Child in a Landscape* NG 713	early 16th century	Pink of Virgin's cloak	Brazilwood + madder
Gerard David	*The Virgin and Child with Saints and Donor* NG 1432	probably 1510	Purple of cloth of honour	Kermes + cochineal (Old World insect source)
Ambrosius Benson	*The Magdalen Reading* NG 655	*c.*1525	Red of the Magdalen's robe	Kermes + trace cochineal
GERMAN SCHOOLS				
Stephan Lochner	*Saints Matthew, Catherine of Alexandria and John the Evangelist* NG 705. Reverse: *Saint Jerome, a female martyr, Saint Gregory the Great and a Donor*	*c.*1445	Red glaze of Saint Jerome's pinkish-red cloak	Probably kermes
Master of Liesborn	*Saints Cosmas and Damian and the Virgin* NG 261	probably 1470–80	Red glaze of Saint Damian's robe, bottom edge	Probably madder
Attributed to the **Master of Liesborn**	*The Crucifixion with Saints* NG 262	*c.*1465–90	Red glaze of drapery, second figure from left	Probably madder
Master of the Aachen Altarpiece	*The Crucifixion* NG 1049	*c.*1495–1505	Red glaze of skirt of kneeling woman left, from left-hand edge	Probably largely kermes[99]
Attributed to **Albrecht Dürer**	*The Painter's Father* NG 1938	1497	Pink background, left-hand edge (after extraction of paint medium)	Madder
Master of the Saint Bartholomew Altarpiece	*Saints Peter and Dorothy* NG 707. Reverse: *Saint John the Evangelist and the Virgin and Child*	probably 1505–10	Red glaze of shadow on Saint John's left sleeve	Probably madder[100]

Artist	Title of Painting	Date	Sample	Dyestuff
Hans Holbein the Younger	*'The Ambassadors'* NG 1314	1533	Pink of Jean de Dinteville's left sleeve	Lac[101]
Dutch School				
Hendrick ter Brugghen	*Jacob reproaching Laban for giving him Leah in place of Rachel* NG 4164	1627	Red glaze of Jacob's waist band	Cochineal (New World)
Rembrandt, Follower	*A Young Man and a Girl playing Cards* NG 1247	perhaps *c.*1645–50	Red glaze of girl's skirt	Cochineal (New World)[102]
Jan Jansz. Treck	*Vanitas Still Life* NG 6533	1648	Shadow on red stripe of cloth	Cochineal (source unclear)
Flemish School				
Anthony van Dyck	*Charity* NG 6494	*c.*1627–8	Cherry-coloured glaze of drapery, from left-hand edge	Cochineal (source unclear)
Peter Paul Rubens	*Minerva protects Pax from Mars ('Peace and War')* NG 46	1629–30	Glaze on Pax's red drapery	Probably cochineal + madder[103]
French School				
Master of Moulins (Jean Hey)	*Charlemagne, and the Meeting of Saints Joachim and Anne at the Golden Gate* NG 4092	*c.*1500	Glaze of Joachim's red hat Charlemagne's pink cloak	Madder Probably madder
Philippe de Champaigne	*Cardinal Richelieu* NG 1449	*c.*1637	Shadow in fold of dark red robe (after extraction of paint medium)	Lac
Pierre Mignard	*The Marquise de Seignelay and Two of her Children* NG 2967	1691	Red drapery of younger child, right	Cochineal (New World)
Maurice-Quentin de La Tour	*Henry Dawkins* NG 5118	*c.*1750	Red coat, from lower edge	Cochineal (New World)[104]
Paul Delaroche	*The Execution of Lady Jane Grey* NG 1909	1833	Red glaze of brocade dress on attendant's lap Red glaze of shadow on executioner's calf	Cochineal (New World)[105] Cochineal (New World)
Gustave Moreau	*Saint George and the Dragon* NG 6436	1889–90	Red drapery falling across horse's back	Cochineal (New World)
English School				
Sir Joshua Reynolds	*Anne, Countess of Albemarle* NG 1259	probably 1759–60	Red glaze on curtain, left-hand side	Cochineal (probably New World)[106]
Thomas Gainsborough	*Mrs Siddons* NG 683	*c.*1783–5	Red of shawl, right-hand side	Cochineal (New World)[107]
Sir Thomas Lawrence	*Queen Charlotte* NG 4257	1789–90	Glaze on brownish-red foliage, left-hand edge	Probably cochineal (New World)
Joseph Mallord William Turner	*Ulysses deriding Polyphemus* NG 508	1829	Red of edge of ship	Cochineal (New World)

Notes and References

1. H. Davy, 'Some experiments and observations on the colours used in painting by the Ancients', *Philosophical Transactions of the Royal Society*, 105, 1815, pp. 97–124, especially pp. 113–16.
2. Davy, ibid., pp. 99–100, 115. See also J. Chaptal, 'Sur quelques couleurs trouvées à Pompeia', *Annales de chimie*, 70, 1809, pp. 22–31.
3. J. Kirby, 'The Preparation of Early Lake Pigments: A Survey', *Dyes on Historical and Archaeological Textiles*, 6, 1987, pp. 12–18 (renamed *Dyes in History and Archaeology* from Vol. 7 onwards); I. Stössel, *Rote Farblacke in der Malerei: Herstellung und Verwendung im deutschsprachigen Raum zwischen ca.1400 und 1850*, Diplomarbeit, Institut für Technologie der Malerei der Staatlichen Akademie der Bildenden Künste, Stuttgart 1985. For the history, biology and general use of the dyes see F. Brunello, *L'Arte della tintura nella storia dell'umanità*, Vicenza 1968 (English edn. Vicenza 1973); D. Cardon, *Guide des teintures naturelles: plantes, lichens, champignons, mollusques et insectes*, Neuchâtel 1990; D. Cardon, *Les 'vers' du rouge: insectes tinctoriaux (Homoptera: Coccoidea) utilisés dans l'Ancien Monde au Moyen-Age*, Paris 1990 (Cahiers d'Histoire et de Philosophie des Sciences, n.s. no. 28, produced by the Société Française d'Histoire des Sciences et des Techniques); R.A. Donkin, 'The Insect Dyes of Western and West Central Asia', *Anthropos: International Review of Ethnology and Linguistics*, 72, 1977, pp. 847–80; R.A. Donkin, 'Spanish Red: An Ethnographical Study of Cochineal and the Opuntia Cactus', *Transactions of the American Philosophical Society (N.S.)*, 67, 5, 1977, pp. 5–84; H. Schweppe, *Handbuch der Naturfarbstoffe; Vorkommen; Verwendung; Nachweis*, Landsberg/ Lech 1993; A. Verhecken and J. Wouters, 'The Coccid Insect Dyes: Historical, Geographical and Technical Data', *Bulletin de l'Institut Royal du Patrimoine Artistique*, XXII, 1988/89, pp. 207–39.
4. Habotai medium weight silk, supplied by Whaleys (Bradford) Ltd, was dyed using a mordant of aluminium potassium sulphate, $AlK(SO_4)_2.12H_2O$ (25%). The wool used was $6^1/_2$ cut KB undyed, oiled, supplied by J. Hyslop Bathgate & Co., Galashiels. The oil was removed by scouring in Decon 90; the wool was then rinsed well and a mordant of 8% aluminium potassium sulphate, 7% potassium hydrogen tartrate, $KO_2CCH(OH)CH(OH)CO_2H$, was used for dyeing: see G. Dalby, *Natural Dyes, Fast or Fugitive*, Alcombe 1985, for method. The preparation of the pigments is discussed in J. Kirby, 'A Spectrophotometric Method for the Identification of Lake Pigment Dyestuffs', *National Gallery Technical Bulletin*, 1, 1977, pp. 35–45, especially pp. 37–8, and D. Saunders and J. Kirby, 'Light-induced Colour Changes in Red and Yellow Lake Pigments', *National Gallery Technical Bulletin*, 15, 1994, pp. 79–97, especially pp. 83–4, 96–7. The kermes lake illustrated was prepared from clippings of dyed wool.
5. A. Wallert, '"Cimatura de grana": Identification of Natural Organic Colorants and Binding Media in Mediaeval Manuscript Illumination', *Zeitschrift für Kunsttechnologie und Konservierung*, 5, 1, 1991, pp. 74–83.
6. J.S. Remington and W. Francis, *Pigments: Their Manufacture, Properties and Use*, London 1954, pp. 193–4.
7. For example, see M. Saltzman, 'The Identification of Dyes in Archaeological and Ethnographic Textiles', *Archaeological Chemistry*, II; edited by G.F. Carter, Washington 1978, pp. 172–85; M. Saltzman, A.M. Keay and J. Christensen, 'The Identification of Colorants in Ancient Textiles', *Dyestuffs*, 44, 8, 1963, pp. 241–51; M. Whiting, 'The Identification of Dyes in Old Oriental Textiles', *ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1–8 October, 1978: Preprints*, Zagreb 1978, pp. 78/9/2/1–9; R. Kumar, F.W. Billmeyer, Jr, and M. Saltzman, 'Identification of Organic Pigments in Paints', *Journal of Coatings Technology*, 57, 1985, pp. 49–54. (The paper discusses the application of the method to modern synthetic pigments.)
8. A. Wallert, 'Fluorescent assay of quinone, lichen and redwood dyestuffs', *Studies in Conservation*, 31, 1986, pp. 145–55.
9. Wallert, 1991, cited in note 5.
10. N.F. Barnes, 'A Spectrophotometric Study of Artists' Pigments', *Technical Studies in the Field of the Fine Arts*, VII, 3, 1939, pp. 120–38; D.R. Duncan, 'The Identification and Estimation of Pigments in Pigmented Compositions by Reflectance Spectrophotometry', *Journal of the Oil and Colour Chemists' Association*, 45, 1962, pp. 300–24; B. Guineau, 'Non-destructive analysis of organic pigments and dyes using Raman microprobe, microfluorometer or absorption microspectrophotometer', *Studies in Conservation*, 34, 1989, pp. 38–44; D.R. Cousins, C.R. Platoni and L.W. Russell, 'The use of microspectrophotometry for the identification of pigments in small paint samples', *Forensic Science International*, 24, 1984, pp. 183–96; C. Binant, 'Application de la microspectrophotométrie de réflexion diffuse à l'analyse de pigments de quinacridones', *Pigments et colorants de l'Antiquité et du Moyen Age* (proceedings of an international colloquium of the Centre National de la Recherche Scientifique, Orléans, 5-8 December 1988), Paris 1990, pp. 156–62.

11. Kirby, 1977, cited in note 4. The method is still in use with modified equipment.
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13. S. Shimoyama and Y. Noda, 'Non-destructive Determination of Natural Dyestuffs used for Ancient Coloured Cloths using a Three-Dimensional Fluorescence Spectrum Technique', *Dyes in History and Archaeology*, 12, 1993, pp. 45–56.
14. M.J.D. Low and N.S. Baer, 'Application of infrared Fourier transform spectroscopy to problems in conservation', *Studies in Conservation*, 22, 1977, pp. 116–28; R.D. Gillard, S.M. Hardman, R.G. Thomas and D.E. Watkinson, 'The detection of dyes by FTIR microscopy', *Studies in Conservation*, 39, 1994, pp. 187–92.
15. W.G.Th. Roelofs, P.H. Hallebeek, J.H. Hofenk de Graaff and R.F.S. Karreman, 'The analysis of natural dyestuffs and organic pigments: A comparative study into the possibilities and limits of various methods', *ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, Australia, 6–11 September, 1987: Preprints*, edited by K. Grimstad, Malibu 1987, pp. 709–17.
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20. Stössel, 1985, cited in note 3, pp. 128–39; *A Closer Look: Technical and Art-Historical Studies on Works by Van Gogh and Gauguin*, edited by C. Peres, M. Hoyle and L. van Tilborgh, Zwolle 1991; the results of examination of lake pigments used by Vincent van Gogh, by J.H. Hofenk de Graaff and others, are described on pp. 75–85; N. Eastaugh, 'Chromatography and Art History', *Chromatography and Analysis*, 19, October 1991, pp. 5–7; see also J.H. Townsend, 'The materials of J.M.W. Turner: pigments', *Studies in Conservation*, 38, 1993, pp. 231–54.
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25. Wouters, 1990, cited in note 23, p. 62; using the computerised diode-array detector, the limit of detection claimed is 10ng carminic acid, compared with about 100ng carminic acid for the system described.
26. Wouters and Verhecken, 1989, cited in note 22, p. 394.
27. Schweppe, 1989, cited in note 19, pp. 201–2; Wouters and Verhecken, 1989, cited in note 21, p. 190.
28. *Handbook of Derivatives for Chromatography*; edited by K. Blau and J. Halket, 2nd edn., Chichester 1993, p. 15.
29. R. White and J. Pilc, 'Analyses of Paint Media', in this *Bulletin*, p. 95.
30. The taxonomy of lac insects is complex; the *Kerria lacca* Kerr group is the commonest and most widely distributed, occurring in India, Pakistan, Nepal and Sri Lanka. The *Kerria greeni* Chamberlin group of species occurs in Burma, Indonesia, Malaysia and Australia. See R.K. Varshney, 'A Review of the Family Tachardiidae (Kerriidae) in the Orient (Homoptera: Coccoidea)', *Oriental Insects*, 18, 1984, pp. 361–84.
31. The standards used in the National Gallery laboratory were supplied by Professor K. Schofield of Exeter University, are labelled A_1 and B, and are impure: see R. Burwood, G. Read, K. Schofield and D.E. Wright, 'The Pigments of Stick Lac. Part I. Isolation and Preliminary Examination', *Journal of the Chemical Society*, 1965, pp. 6067–73; R. Burwood et al., 'The Pigments of Stick Lac. Part II. The Structure of Laccaic acid A_1', *Journal of the Chemical Society (C)*, 1967, pp. 842–51. The structure of laccaic acid A elucidated by Professor Venkataraman's group at the National Chemical Laboratory, Poona, is identical to A_1; the same group have published the structure for laccaic acid B, but unfortunately could not supply the authors with any for use as a standard. See E.D. Pandhare, A.V. Rama Rao and I.N. Shaik, 'Lac Pigments: Part III – Isolation of Laccaic Acids A and B and the Constitution of Laccaic Acid A', *Indian Journal of Chemistry*, 7, 1969, pp. 977–86; N.S. Bhide, E.D. Pandhare, A.V. Rama Rao, I.N. Shaik and R. Srinivasan, 'Lac Pigments: Part IV – Constitution of Laccaic Acid B', ibid., pp. 987–95.
32. M. Wyld, A. Roy and A. Smith, 'Gerard David's "The Virgin and Child with Saints and a Donor"', *National Gallery Technical Bulletin*, 3, 1979, pp. 51–65, especially p. 62; Donkin, 'Spanish Red: An Ethnographical Study of Cochineal and the Opuntia Cactus', 1977, cited in note 3, pp. 23–4, 37.
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34. *The Flavonoids*, ed. J.B. Harborne, T.J. Mabry and H. Mabry, London 1975, pp. 817, 853–4; Schweppe, 1993, cited in note 3, pp. 412–16, 420–1. For the chemistry of the anthraquinone dyestuffs, see R.H. Thomson, *Naturally Occurring Quinones*, 2nd edn., London 1971, and *Naturally Occurring Quinones III: Recent Advances*, London 1987 (the 3rd edn. updates, but does not replace the 2nd.).
35. For the laccaic acid standards see note 31 above. Alizarin, purpurin and carminic acid were supplied by Aldrich Chemical Co. Ltd, Gillingham, Dorset. Flavokermesic acid was supplied by Dr J. Wouters, Koninklijk Instituut voor het Kunstpatrimonium, Brussels. Kermesic acid was identified by UV-visible spectroscopy.
36. Pseudopurpurin, 1,2,4-trihydroxyanthraquinone-3-carboxylic acid, is present in the root, largely in the form of galiosin (pseudopurpurin-1-ß-D-primveroside), which may be responsible for a peak eluted at about 139 minutes. It may be converted to purpurin by decarboxylation as the ground root is stored and exposed to the air. Schweppe, 1993, cited in note 3, pp. 230, 240; ibid., 1989, cited in note 19, pp. 193, 201–3.

37. R.K. Varshney, 'Taxonomic Studies on Lac Insects of India', *Oriental Insects*, Supplement 5, 1976, pp. 1–97, especially pp. 42–3; M.E. Ali, D.C. Das, M.I.H. Khan and K. Ahmed, 'Investigation on Lac. Part V. Effect on the Composition of Lac due to Change of Host Plants of Lac Insect', *Bangladesh Journal of Scientific and Industrial Research*, 14, 1–2, 1979, pp. 286–8.
38. Wouters and Verhecken, 1989, cited in note 22; A.R. Burnett and R.H. Thomson, 'Naturally Occurring Quinones. Part XV. Biogenesis of the Anthraquinones in *Rubia tinctorum* L. (Madder)', *Journal of the Chemical Society* (C), 1968, pp. 2437–41.
39. J.P. Breynius, *Historia naturalis cocci radicum tinctorii, quod polonicum vulgo audit; praemissis quibusdam coccum in genere et in specie coccum ex ilice, quod grana kermes et alterum Americanum, quod cochinilla hispanis dicitur spectantibus*, Gdansk 1731, plates and caption (unnumbered) at end of text.
40. G. Taylor, 'Insect Red Dyes: An Update', *Dyes on Historical and Archaeological Textiles*, 6, 1987, pp. 21–4; Wouters and Verhecken, 1989, cited in note 22, pp. 400–2, 407. For the distribution of the principal Old World cochineal insects see Donkin, 'The Insect Dyes of Western and West Central Asia', 1977, cited in note 3, p. 848. There are other, less well-known, Old World scale insects found in parts of Eastern Europe and the Near East which may have been used locally for dyeing: see Cardon, *Guide des teintures naturelles*, 1990, cited in note 3, pp. 361–2, 377–8; Wouters and Verhecken, 1991, cited in note 22, p. 21.
41. Wouters and Verhecken, 1989, cited in note 22, pp. 402–4, 406–7.
42. Brazilwood was tentatively identified in one sample, from the striped sash of a woman on the extreme left of Veronese's *The Family of Darius before Alexander* (NG 294), dated 1565–70, by TLC in 1977 and microspectrophotometry in 1994. Microspectrophotometric examination of other samples of red lake pigment from the painting suggested the presence of a scale insect dyestuff; in other works by Veronese in the National Gallery cochineal-containing lakes have been found, as Table 2 shows. See N. Penny and M. Spring, 'Veronese's Paintings in the National Gallery. Technique and Materials: Part I', *National Gallery Technical Bulletin*, 16, 1995, pp. 4–29, especially pp. 21–2.
43. Hofenk-de Graaff and Roelofs, 1972, cited in note 19, p. 25. It is clear that the dyestuff was considered to be of lower quality, however much it may have been used. The statutes of the Venetian dyers' guild of 1243 include a stricture against its use without permission; a similar stricture (also applying to madder) appears in the statutes of the Lucca dyers' guild of 1255. This is a typical example of a prohibition against the substitution of a cheaper material for a more expensive one: in the Florentine painters' guild regulations of 1315–16, for example, the substitution of azurite for ultramarine is forbidden. Brazilwood's poor light-fastness would have been one factor behind the regulation. See Brunello, 1968, cited in note 3, pp. 140–4; D. Bomford, J. Dunkerton, D. Gordon, A. Roy and J. Kirby, *Art in the Making: Italian Painting before 1400*, London 1989, pp. 6–7, 213–14.
44. W. Cholmeley, 'The Request and Suite of a True-Hearted Englishman, written by William Cholmeley, Londyner, in the year 1553', edited by W.J. Thomas, in *Tudor Economic Documents*, edited by R.H. Tawney and E. Power, 3 vols., London 1924 (1951 reprint), Vol. III, no. 5, pp. 130–48, especially pp. 137, 139.
45. Hofenk-de Graaff and Roelofs, 1972, cited in note 19; W.G.Th. Roelofs and J.H. Hofenk de Graaff, 'Analisi delle materie coloranti', *Botticelli e il ricamo del Museo Poldi Pezzoli: Storia di un restauro*, Milan *c.*1990, pp. 87–93; L. Masschelein-Kleiner and L. Maes, 'Etude technique de la tapisserie tournaisienne aux XV^{e} et XVI^{e} siècles. Les colorants', *Bulletin de l'Institut Royal du Patrimoine Artistique*, XII, 1970, pp. 269–79; 'Etude technique de la tapisserie des Pays-Bas méridionaux. Les tapisseries anversoises des XVI^{e} et XVII^{e} siècles. Les teintures', *Bulletin de l'Institut Royal du Patrimoine Artistique*, XVI, 1976/77, pp. 143–53; J. Wouters, 'Analyse des colorants des tapisseries brugeoises des XVI^{e} et XVII^{e} siècles' in G. Delmarcel and E. Duverger, *Bruges et la tapisserie*, Bruges 1987, pp. 515–26. It is worth noting that Southern Europe, notably Italy, was for many years the source of fine silks, while the wool industry was at the same time of similar importance in Northern Europe.
46. Brunello, 1968, cited in note 3, pp. 143–4; Francesco Balducci Pegolotti, [*Libro di divisamenti di paesi e di misuri di mercatanzie e d'altre cose bisogneroli di sapere a' mercatanti*, c. 1339–40] *La pratica della mercatura*, edited by A. Evans, Cambridge, Mass. 1936, p. 371; A. Nannizzi, *L'Arte degli Speziali in Siena*, Siena 1939, p. 43. Madder was cultivated in Lombardy and other parts of Italy. It should be remembered that leather was also dyed, using the same dyestuffs; brazilwood and madder are mentioned in this context: see, for example, *Segreti per colori*; the Bolognese manuscript (Bologna, Biblioteca dell'Università, MS 2681, fifteenth century) in M.P. Merrifield, *Original Treatises dating from the XIIth to the XVIIIth centuries on*

the Arts of Painting, London 1849 (Dover reprint, New York and London 1967), Vol. II, no. 110, pp. 546–57.

47. Masschelein-Kleiner and Maes, 1976/77, cited in note 45; G. Rosetti, [*Plictho de larte de tentori*] *The Plictho of Gioanventura Rosetti*, trs. S.M. Edelstein and H.C. Borghetty, Cambridge, Mass. and London 1969 (includes facsimile of 1st edn., Venice 1548), pp. 18, 107–8 (for example).
48. L. Guicciardini, *Descrittione di M. Lodovico Guicciardini patritio fiorentino, di tutti i paesi bassi, altrimenti detti Germania inferiore*, Antwerp 1567, pp. 60–115, 119–20; *Tarifa zoè noticia dy pexi e mexure di luoghi e tere che s'adovra marcadantia per el mondo*, [later fourteenth or early fifteenth century], R. Istituto Superiore di Scienze Economiche e Commerciale de Venezia, Venice 1925; L. Lazzarini, 'Il colore nei pittori veneziani tra il 1480 e il 1580', *Bollettino d'Arte*, supplement 5, 1983, pp. 135–44, especially pp. 135–6.
49. Sanyova and Wouters, 1993, cited in note 24, pp. 39–41.
50. J. Decaisne, 'Recherches anatomiques et physiologiques sur la garance', *Mémoires couronnés par l'Académie Royale des Sciences et Belle-lettres de Bruxelles*, 12, 1837 (2nd essay); see plate 6. The authors are grateful to Dr David Hill, Department for Continuing Education, University of Bristol, for bringing this reference to their attention.
51. P. Miller, *The Method of Cultivating Madder, as it is now practised by the Dutch in Zealand ...*, London 1758, pp. 10–11; C. Wiskerke, 'De geschiedenis van het meekrapbedrijf in Nederland', *Economisch-Historisch Jaarboek*, XXV, 1952, pp. 1–144; see pp. 44–9, especially Plate V.
52. G.A. Fokker, 'De oudst bekende keur op het bereiden van en den handel in meekrap in Zeeland', *Archief Vroegere en Latere Mededeelingen Voornamelijk in Betrekking tot Zeeland*, II, 1866–69, vi, pp. 317–28. The authors are grateful to Dr Lorne Campbell for this reference.
53. Wiskerke, 1952, cited in note 51; G. Asaert, 'Handel in kleurstoffen op de Antwerpse markt tijdens de XVe eeuw', *Bijdragen en Mededelingen betreffende de geschiedenis der Nederlanden*, 88, 3, 1973, pp. 377–402.
54. P.J. Garidel, *Histoire des plantes qui naissent aux environs d'Aix et des plusieurs autres endroits de la Provence*, Aix 1715, pp. 247–55; plate 53 (following p. 260).
55. Wouters and Verhecken, 1991, cited in note 22, pp. 219–20; Sanyova and Wouters, 1993, cited in note 24, pp. 40–1.
56. Pegolotti/Evans, 1936, cited in note 46, p. 297; G. Gargiolli, *L'Arte della seta in Firenze; trattato del secolo XV*, Florence 1868, p. 109; varieties of *chermisi* are also listed. Several fifteenth and sixteenth-century manuscripts of the treatise exist; the most complete version is one in the Biblioteca Riccardiana, Florence, MS 2580. Gargiolli thought all were copies of a lost original dating from the end of the fourteenth or early fifteenth century. See also A. Doren, *Studien aus der Florentiner Wirtschaftsgeschichte*, Vol. 1: *Die florentiner Wollentuchindustrie vom vierzehnten bis zum sechszehnten Jahrhundert*, Stuttgart 1901, pp. 484–93
57. Rosetti, 1548 (1969 reprint), cited in note 47: *grana*, pp. 5–6, 94; 45, 136; *cremesino*, pp. 47, 138–9.
58. Gargiolli, 1868, cited in note 56, p. 78.
59. Verhecken and Wouters, 1988/89, cited in note 3, pp. 226–9.
60. Pegolotti/Evans, 1936, cited in note 46, pp. 361, 366, 371, 382–3. Similar, less detailed, descriptions are found in later merchants' handbooks.
61. [The *Nürnberger Kunstbuch*, Nürnberger Stadtbibliothek, MS cent. VI, 89, mid-fifteenth century] E.E. Ploss, *Ein Buch von alten Farben: Technologie der Textilfarben im Mittelalter mit einem Ausblick auf die festen Farben*, Heidelberg and Berlin 1962, p. 113; *Middelnederlandse verfrecepten voor miniaturen en 'alderhande substancien'*, ed. W.L. Braekman, Brussels 1986 (SCRIPTA Mediaeval and Renaissance Texts and Studies, Vol. 18, published by the Research Center of Mediaeval and Renaissance Studies, Brussels): Text I (MS 517, Wellcome Historical Medical Library, London, late fifteenth century, extracts), no. 45, pp. 46–7 ; Text II, (*T'Bouck van Wondre*, Brussels 1513), no. 9 (on dyeing '*vlocken*'), p. 66; *Instruction générale pour la teinture des laines*, Paris 1671, pp. 24–5, 31, 73.
62. Braekman, 1986, ibid., Text I, no. 45, pp. 46–7; Ploss, 1962, ibid., pp. 113–14.
63. P. de La Hyre, 'Traité de la pratique de peinture', *Mémoires de l'Académie Royale des Sciences depuis 1666 jusqu'à 1699*, IX, Paris 1730, pp. 637–730; see p. 670. (Published posthumously; based on a lecture given to the Académie in 1709.)
64. *Segreti per colori* [the Bolognese manuscript], Merrifield Vol. II, 1849, cited in note 46, no. 110, pp. 432–5. In other recipes (B.139, pp. 456–7) it appears that the alkali was stronger and that the fibres dissolved to a large extent. See also Wallert, 1991, cited in note 5, p. 82, note 5.
65. U. Birkmaier, A. Wallert and A. Rothe, 'Technical Examination of Titian's *Venus and Adonis*: A Note on Early Italian Oil Painting Technique', *Historical Painting Techniques, Materials and Studio Practice: Preprints of a Symposium, University of Leiden, the Netherlands, 26-29 June 1995*, edited by

A. Wallert, E. Hermens and M. Peek, Malibu 1995, pp. 117–26, especially p. 123.
66. J. Murrell, 'John Guillim's Book: A Heraldic Painter's *Vade Mecum*', *The Walpole Society*, LVII, 1993/94, pp. 1–51, especially p. 25: 'To Make a Red Rose'. (National Art Library MS L. 1774-1935, press mark 86. EE. 69.)
67. J. Plesters and L. Lazzarini, 'I materiali e la tecnica del Tintoretto della Scuola di San Rocco', *Atti di Convegno Internazionale di Studi su Jacopo Tintoretto nel IV centennario della morte, Venice 1994*, in press.
68. Kirby, 1977, cited in note 4, pp. 40, 42; C. Brown and A. Roy, 'Rembrandt's "Alexander the Great"', *Burlington Magazine*, CXXXIV, no. 1070, 1992, pp. 286–97, especially pp. 291, 293–4.
69. J.H. Hofenk de Graaff, '"Woven Bouquet": Dyestuff-Analysis on a Group of Northern Dutch flowered Table-cloths and Tapestries of the 17th Century', *ICOM Committee for Conservation, 4th Triennial Meeting, Venice, 13-18 October, 1975: Preprints*, Venice 1975, pp. 75/10/3/1–15; [D.W.S.d.H.n., *Dat oprecht secreet van dat roet scherlaeken met sijn apendicht* ..., 1631] N.W. Posthumus and W.L.J. de Nie, 'Een Handschrift over de textielververij in de Republiek uit de eerste helft der zeventiende eeuw', *Nederlandsch Economisch-Historisch Archief Jaarboek*, XX, 1936, pp. 212–57, especially pp. 234–7, 244. Posthumus identifies the author of the manuscript, which is in the Economisch-Historisch Bibliotheek, Amsterdam, as Dirc Willemsz. van der Heyden.
70. F. Pritchard, 'Dyes on some 16th- and 17th-century textiles excavated in London', *Dyes in History and Archaeology*, 10, 1991, pp. 38–41
71. For an account of this analysis see Claire Chorley, *The Cleaning and Restoration of William Larkin's Portrait of Susan Villiers, Countess of Denbigh*, unpublished essay for the Conservation of Easel Paintings course, Hamilton Kerr Institute, University of Cambridge. Thanks are due to Ian McClure and Renate Woudhuysen Keller for permission to publish this result.
72. Sanyova and Wouters, 1993, cited in note 24, pp. 39–41.
73. See, for example, Rosetti, 1548 (1969 reprint), cited in note 47, pp. 20, 110; 28, 118; 36, 127–8; 62–3, 155–6
74. See, for example, Rosetti, ibid., pp. 23–4, 114; 28, 118; *Instruction générale pour la teinture des laines*, cited in note 61, p. 24.
75. Gargiolli, 1868, cited in note 56, pp. 33, 56, 69, 134; Rosetti, ibid., pp. 44–6, 134–7; 50–51, 142–3; 53–4, 145–7; Verhecken and Wouters, 1988/89, cited in note 3, pp. 215–16, 227.
76. Pegolotti/Evans, 1936, cited in note 46, p. 366; Cardon, *Les 'vers' du rouge*, 1990, cited in note 3, pp. 110–12.
77. Garcia da Orta, *Colloquies on the Simples and Drugs of India*, edited and annotated by the Conde de Ficalho, translated by Sir Clements Markham, London 1913, pp. 240–50 (first edn. Goa 1563).
78. E. Bancroft, *Experimental Researches concerning the Philosophy of Permanent Colours*..., 2 vols., London 1813, Vol. II, pp. 1–59.
79. La Hyre, 1730, cited in note 63, pp. 670–2; H. Gautier, *L'Art de laver, ou Nouvelle manière de peindre sur le papier*, Lyon 1687 (facsimile reprint Portland, Oreg. 1972), pp. 49–52. With the chromatographic system described, no distinction between cochineal carmine and cochineal lake can be made.
80. J. Dunkerton and A. Roy, 'The Materials of a Group of late Fifteenth-century Florentine Panel Paintings', in this *Bulletin*, pp. 20–31, especially p. 28; J. Dunkerton, 'The Painting Technique of the Manchester Madonna' in M. Hirst and J. Dunkerton, *Making and Meaning: The Young Michelangelo*, exhibition catalogue, London 1994, pp. 83–105. In the case of the Michelangelo painting, the presence of a trace of kermes lake was suspected, but could not be confirmed.
81. P. Bensi, 'Gli Gesuati dell'arte. I Gesuati di San Giusto alle Mura e la pittura del rinascimento a Firenze', *Studi di Storia delle Arti*, 1980, pp. 33–47, especially p. 41.
82. Neri di Bicci, *Le ricordanze (10 marzo 1453 – 24 aprile 1475)*, edited by Bruno Santi, Pisa 1976, pp. 270, 279, 316–18, 328, 366. The Florentine ounce was equivalent to *c*.28.3g; there were 12 ounces to the pound in Italy: see Bomford et al., 1989, cited in note 43, pp. 205–6.
83. Lorenzo Lotto, *Il 'Libro di spese diverse' con aggiunta di lettere e d'altri documenti*, edited by P. Zampetti, Venice and Rome 1969, p. 238; an even more expensive lake, from the Bolognese architect Sebastiano Serlio, is mentioned on p. 234. The portrait may be that referred to on p. 98.
84. Wallert, 1991, cited in note 5, pp. 79–81.
85. J. Hellot, *L'art de la teinture des laines et les étoffes de laine en grand et petit teint*, Paris 1750, pp. 244–5; R. Blanchard, *Les coccidés utiles: Thèse présentée au concours d'agrégation (Anatomie, Physiologie et histoire naturelle), Faculté de Médecine de Paris*, Meulan 1883, pp. 56–7; W. Born, 'Scarlet', *Ciba Review*, 7, 1938, pp. 206–27, especially pp. 212–14.
86. Blanchard, ibid., pp. 58–60.
87. Chr.H. Schmidt, *Vollständiges Farben-Laboratorium*, 2nd edn., Weimar 1847 (1st edn. 1841), pp. 454–6; G. Field, *Examples and Anecdotes of Pigments. Practical Journal 1809*, f. 332. Field Manuscripts, Field/6, photographic copy, Courtauld Institute Library, London.

88. L. Keith and A. Roy, 'Giampietrino, Boltraffio and the Influence of Leonardo', in this *Bulletin*, pp. 4–19, especially note 39, p. 19.
89. Red glaze on the Virgin's robe in *The Coronation of the Virgin* (NG 1897), the central panel of the altarpiece of which NG 216 forms a part, was thought to contain lac lake, but it could be examined by microspectrophotometry only; see A. Burnstock, 'The Fading of the Virgin's Robe in Lorenzo Monaco's "Coronation of the Virgin"', *National Gallery Technical Bulletin*, 12, 1988, pp. 58–65.
90. Examination by TLC suggested that lac lake had been used; it must be assumed that the kermes dyestuff present had been altered beyond recognition by the boron trifluoride reagent as described in the text. The glaze, in an egg tempera medium, is painted over silver leaf; both silver and glaze have deteriorated, but the chemical effect on the dyestuff has not been elucidated: see D. Bomford and J. Kirby, 'Giovanni di Paolo's "SS. Fabian and Sebastian"', *National Gallery Technical Bulletin*, 2, 1978, pp. 56–65 and Plate 8, pp. 46–7, especially pp. 64–5 and Plate 8a.
91. This confirms the result obtained by TLC in 1977.
92. Penny and Spring, 1995, cited in note 42, p. 15 and note 51, p. 27.
93. For a discussion of Veronese's *Allegories* and *The Adoration of the Kings*, see N. Penny, A. Roy and M. Spring, 'Veronese's Paintings in the National Gallery. Technique and Materials: Part II', in this *Bulletin*, pp. 32–55, especially p. 49.
94. Lac lake was identified in samples from Jupiter's cloak and the drapery over the bed by TLC: see J. Plesters, 'Tintoretto's Paintings in the National Gallery', *National Gallery Technical Bulletin*, 4, 1980, pp. 32–47, especially p. 39 (compare results from NG 1130, *Christ washing his Disciples' Feet*, p. 37).
95. This painting was formerly ascribed to Murillo.
96. It seems likely that the work now visible has been painted over an earlier, seventeenth-century composition, perhaps a version of the same subject: see M. Levey, *National Gallery Catalogues: 17th and 18th Century Italian Schools*, London 1971, p. 192. The sample examined was from the lower, seventeenth-century, paint. Carminic acid was found to be present, but the insect source could not be determined because of interference from other organic components.
97. The presence of madder dyestuff in addition to that extracted from kermes could not be confirmed.
98. Madder alone appeared to be present in a sample taken from the red paint of the carpet in the companion panel, *The Mass of Saint Giles* (NG 4681), examined by microspectrophotometry and TLC; see D. Bomford and J. Kirby, 'Two Panels by the Master of Saint Giles', *National Gallery Technical Bulletin*, 1, 1977, pp. 46–56, especially p. 55.
99. The chromatogram also revealed the presence of alizarin crimson retouching.
100. The presence of kermes dyestuff in addition to the madder could not be confirmed.
101. This result may appear unusual in a Northern European context; the picture was painted in London, however, and there are no analytical results from English paintings of this period for comparison.
102. R. White and J. Kirby, 'Rembrandt and his Circle: Seventeenth-Century Dutch Paint Media Re-examined', *National Gallery Technical Bulletin*, 15, 1994, pp. 64–78, especially p. 73, Plate 2, p. 66 and note 60, p. 77.
103. The sample was extremely small and contained much drying oil, obscuring the chromatogram to such an extent that it is not possible to rule out the presence of lac lake; cochineal lake was identified in Rubens's *Elevation of the Cross*; see Wouters, 1992, cited in note 24, p. 82.
104. J. Pilc and R. White, 'The Application of FTIR-Microscopy to the Analysis of Paint Binders in Easel Paintings', *National Gallery Technical Bulletin*, 16, 1995, pp. 73–84, especially pp. 82–3 and Fig. 8, p. 79.
105. J. Kirby and A. Roy, 'Paul Delaroche: A Case Study of Academic Painting', *Historical Painting Techniques, Materials and Studio Practice*, 1995, cited in note 65, pp. 166–75, especially p. 172.
106. Saunders and Kirby, 1994, cited in note 4, pp. 79–97, especially pp. 79–80.
107. Cochineal lake was also identified in the sitter's coat in Gainsborough's *Dr Ralph Schomberg* (NG 684); see D. Bomford, A. Roy and D. Saunders, 'Gainsborough's "Dr Ralph Schomberg"', *National Gallery Technical Bulletin*, 12, 1988, pp. 44–57, especially pp. 51–4.