Archaeological and Anthropological Sciences (2021) 13: 159
https://doi.org/10.1007/s12520-021-01392-3

REVIEW

Pigments—the palette of organic colourants in wall paintings

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Received: 15 January 2021 / Accepted: 30 June 2021 / Published online: 8 September 2021

Abstract

The present contribution deals with the use of organic colourants in wall paintings, polychrome pottery and painted stone artworks, i.e. painted artworks on inorganic supports. The term *organic colourants* is referred to the chemical nature of these compounds but not to the way of application; therefore, organic colourants can be dyes, lakes or pigments. The use of organic colourants in wall paintings has been given little attention in the past, perhaps on the assumption that they were rarely used by ancient artists. Recent diagnostic studies, however, brought evidence that their use was not fragmentary; on the contrary, there seems to be continuity in the centuries, at least with regard to the most widely used such as madder, Tyrian purple and indigo. Sources, alteration phenomena, identification methods and analytical evidence is given for the main organic colourants with concern to red, yellow, green, purple and blue hues. Drawbacks and issues are discussed with concern to the identification techniques.

Keywords Organic · Dyes · Lakes · SERS · FORS · HPLC

Premise

This Topical Collection (TC) covers several topics in the field of study, in which ancient architecture, art history, archaeology and material analyses intersect. The chosen perspective is that of a multidisciplinary scenario, capable of combining, integrating and solving the research issues raised by the study of mortars, plasters and pigments (Gliozzo et al. 2021).

The first group of contributions explains how mortars have been made and used through the ages (Arizzi and Cultrone 2021, Ergenç et al. 2021, Lancaster 2021, Vitti 2021). An insight into their production, transport and on-site organisation is further provided by DeLaine (2021). Furthermore, several issues concerning the degradation and conservation of mortars and plasters are addressed from practical and technical standpoints (La Russa and Ruffolo 2021, Caroselli et al. 2021).

The second group of contributions is focused on pigments, starting from a philological essay on terminology (Becker 2021). Three archaeological reviews on prehistoric (Domingo Sanz and Chieli 2021), Roman (Salvadori and Sbrolli 2021) and Medieval (Murat 2021) wall paintings clarify the archaeological and historical/cultural framework. A series of archaeometric reviews illustrate the state of the art of the studies carried out on Fe-based red, yellow and brown ochres (Mastrotheodoros et al. forthcoming); Cu-based greens and blues (Švarcová et al. 2021); As-based yellows and reds (Gliozzo and Burgio 2021); Pb-based whites, reds, yellows and oranges (Gliozzo and Ionescu 2021); Hg-based red and white (Gliozzo 2021) and organic pigments (this paper). An overview of the use of inks, pigments and dyes in manuscripts, their scientific examination and analysis protocol (Burgio 2021) as well as an overview of glass-based pigments (Cavallo and Riccardi forthcoming) are also presented. Furthermore, two papers on cosmetic (Pérez-Arantegui 2021) and bioactive (antibacterial) pigments (Knapp et al. 2021) provide insights into the variety and different uses of these materials.

This article is part of the Topical Collection on *Mortars, plasters and pigments: Research questions and answers*

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Introduction (terminology, historical context, technical documents, recipes)

The present contribution will deal with the use of organic colourants in wall paintings, encompassing also other painted artworks on inorganic supports such as polychrome pottery and stone artworks. The use of organic colourants in wall paintings has been given little attention, perhaps by the artists who created the paintings, most probably by the scholars who later studied the paintings and by the diagnostics experts who analysed them. There are some reasons for this, that will be dealt with later. Let us firstly give some definitions. The term *organic colourants* refers strictly to the chemical nature of these compounds, irrespective of the way of application: they are composed mainly of organic molecules, that is, compounds of carbon and hydrogen. Despite the difference on the method of application in painting, organic colourants can be either *pigments*, *dyes* or *lakes*:

- A *pigment* is a colourant not soluble in a medium, in which it forms a dispersion; while typically pigments are of inorganic nature, organic compounds not soluble in water can be used as *organic pigments*.
- A *dye* is a colourant soluble in the medium.
- A *lake* is a dye chemically or physically supported on an inorganic base, in such a way that it is not any more soluble in the medium and therefore behaves like a pigment.

Dyes are of vegetal or animal origin, therefore they are intrinsically of organic nature. There are several hundreds of different dyes, some of which were used since at least the second millennium BC (Cardon 2007). While the main application of dyes has always been in textile dyeing, some of them have been used in painting as well, as *juices*, i.e. simple aqueous extracts, or *lakes*, i.e. juices chemically or physically fixed on white inorganic substrates. Lakes are specific to art of painting, but there are strong similarities in the mechanisms of fixing dyes on fabrics to give coloured garments and of fixing dyes on inorganic supports to give lakes: a cation, such as Al^{3+}, is mostly involved as intermediate.

While the groups of dyes and lakes contain several members, very few colourants, among which indigo and Tyrian purple, corresponded to the definition of organic pigments: they are in fact organic materials respectively of vegetal and animal origin, used mainly as textile dyes but insoluble in water (they are in fact *vat dyes*, i.e. they request a preliminary step in which are reduced to soluble forms); therefore, they could be used as pigments in painting art. After the development of the oil industry, however, several organic pigments derived from oil were synthetically created, a remarkable example of which are the copper phthalocyanines.

A marked difference must be highlighted between the use of dyes/lakes from one side, and of organic pigments (indigo and Tyrian purple above all) from the other side: the former have little or no hiding power, so they were used mostly as transparent or translucid glazing, in order to modify the appearance of the macroscopic colours of mineral pigments applied below; the latter have body and higher hiding power, so they were used exactly as any other pigment.

It is well known that the palette used by artists for wall paintings was plenty of mineral pigments such as ochres and earths, but, apart from carbon-based pigments, relatively poor in organic colourants derived from vegetal and animal sources; the oldest organic colourant dye must have been Tyrian purple, the earliest evidence of which is reported in eighteenth to seventeenth century BC Minoan wall paintings, while indigo and madder are attested respectively since thirteenth and eight centuries BC (see later). In comparison, the palette used for panel painting and for miniature painting was far richer in such colourants: *kermes*, *cochineal*, *brazilwood*, *saffron*, *weld, as well as indigo and madder*, were almost indispensable for these artistic formats at least since Egyptian times. Why is this not true for wall paintings? The main reason is that most organic colourants are fugitive, that is they can fade in time due to the action of light and other chemical and biological agents. While this is not an issue for painted artworks intended to be kept indoors, such as illuminated manuscripts and—in part—wood or canvas paintings, it certainly is for artworks intended for open or otherwise illuminated spaces, such as most wall paintings. Already in the end of fouteenth century, Cennino Cennini, in his *Il libro dell'arte* (Frezzato 2009), warned painters against the use of colourants of vegetal or animal origin in wall paintings:

- At chapter XLIV, speaking of a generical lake (it is not clear whether of vegetal or animal origin) he says that "*laccha…s'adopera in muro con tempera; ma l'aria è sua nimica*" ("lake… is used in wall painting with temperas; air is its enemy, however").
- For saffron (chapter XLIX) he states "*…guardi non vegga l'aria, ché subito perde suo colore*", ("be careful that it does not see the air, because it immediately loses its colour").
- As to weld (chapter L), he finally says "*…perde all'aria; non è buono in muro*" ("it loses consistency in the air; it is not good in the wall").

In addition, most dyes and lakes are not compatible with the alkaline medium used in fresco painting. Cennino Cennini advises (chapter LXXII) that "*…in fresco sono colori che non si può lavorare*, *come orpimento*, *cinabro, azzurro* *della Magnia*, *minio, biaccha*, *verderame*, *e laccha*" ("there are colours that cannot be used for fresco, such as orpiment, cinnabar, blue of Magna (i.e. azurite from Alemagna—Germany), red lead, white lead, verdigris, and lake"); the lake cited by Cennini could be either of vegetal or animal origin as said before. This is only a part of the explanation, however, because painters would rarely use 100% true *fresco* painting; in fact, mineral pigments incompatible with alkaline pH, such as lead white or azurite, were however used in wall paintings, only they were used with the appropriate medium Cennini himself, in chapter LXXVII, told "…e nota, che ogni cosa che lavori in fresco vuole essere tratto a fine e ritoccato in secco con tempera" ("and notice that everything you work in *fresco* wants to be fine-tuned and retouched in *secco* with tempera").

On the other hand, the hypothesis, highly popular among scholars from the 1960s onwards, that the ancient wall paintings were by definition *fresco* paintings, has been denied on the basis of accurate diagnostic evidence. Different authors (Brecoulaki et al. 2012; Cuní 2016) brought to light the fact that mostly mixed painting techniques, if not techniques completely based on organic binders, were also used, at least as far as wall paintings from the Late Bronze Age to the Roman era are concerned; the same holds true for most wall paintings created in Asian cultures. A thorough work by Casadio et al. (2004) surveyed the historical information arising from ancient literary sources on the binding media used in wall paintings, and compared it to the analytical evidence arising from modern diagnostic studies. A wide range of organic binders emerged that were cited in the historical sources from Greek-Roman age to the Renaissance, to which relatively few—and mostly recent—diagnostic studies corresponded; this may explain why it was assumed that all wall paintings were created with the *fresco* technique. In the end, then, the use of organic colourants in wall paintings does not appear to have been limited by the binding medium.

Another explanation for the limited use of organic colourants in wall paintings can be commercial: organic colourants were on average more expensive than mineral pigments, so their use on large painted areas, as is the case of wall paintings, was generally unfavourable. Product information can be found in the few literary sources that provide information on the cost of colourants, such as in the *Ricordanze* by Neri di Bicci, artist in Florence in the fifteenth century (Santi 1976): he tells us that red lakes (possibly kermes or other dyes from scale insects) were second in price only to the precious lapis lazuli from Afghanistan and to superior quality azurite, probably due to the difficult and highly specialised production of such colourants. A similar information was reported by Nash (2010) who surveyed the proofs of payment for colourants supplied to the court of the Dukes of Burgundy in the fourteenth to fifteenth century: rose and sinople, two terms that may refer to scale insect dyes and/or to brazilwood, ranked second in price after *Azur d'Acre* (best quality lapis lazuli) and on par with *Azur d'Alemaigne* (azurite). Of course, such assumptions are valid only for the periods for which literary sources are available, and do not necessarily apply to other periods.

For the reasons above explained, it is not surprising that the use of organic colourants in wall paintings has never been given adequate attention. Very few comprehensive reviews exist in the scientific literature. The research carried out by the Getty Conservation Institute in the years 2006–2010 (Grzywacz et al. 2008, 2010, 2011) in collaboration with the Dunhuang Academy (China), surveyed all the biological sources that were used for the production of organic colourants in Asia, identifying not less than 108 items. The information gathered was used to produce reference samples and spectral databases, to improve the diagnostic potential in studying the paintings at the Mogao Caves in Dunhuang, China, as well as in future diagnostic works. This seems to be, to the author's knowledge, the only systematic work on organic colourants.

Nevertheless, the world of organic colourants is worthy of being known also in the case of wall paintings, because it reveals ingenious solutions by the artists of ancient times.

As it will appear later, a survey on the scientific literature will reveal that the use of organic colourants in wall paintings has a longer and wider tradition in Asian cultures that in European ones, probably due to the major availability of raw matters (Grzywacz et al. 2010). Moreover, in some cultures, e.g. Indian and Tibetan, the *buon fresco* painting technique is rarely used in favour of the *secco* technique (Agrawal 1989; Oeter and Skedzuhn-Safir 2015) that allows the use of a larger palette, including organic colourants that cannot withstand the alkaline medium of fresco painting.

Apart from the diagnostic evidences given by chemical analysis, a major part of the information can be drawn from ancient literary sources. As far as European sources are concerned, however, from Antiquity to fourteenth century, we can rely on very few treatises, mostly compilations of complex and anonymous handwritten traditions, often interpolated with other traditions and alchemical practices. The most significant sources containing prescriptions for the preparation of vegetal colourants are as follows:

- *Compositiones Lucenses* or *Compositiones ad tingenda musiva*, Codice n. 490 at Biblioteca Capitolare di Lucca, datable between the end of the eighth century and the beginning of the ninth (Caffaro 2003).
- *De coloribus et artibus Romanorum*, text attributed to Eraclius and datable between the eighth and the ninth century (Garzya Romano 1996).
- *Mappae Clavicula*, datable between the ninth and the twelfth century (Phillipps 1847).

Interesting information, though more oriented towards the use of dyes for textile dyeing, can be found in the following Greek and Latin sources:

- *De architectura* by Marcus Vitruvius Pollio, first century BC to first century AD, in which the Latin author, at book VII, chapter XIV, speaks about some plant colours (De Architectura VII).
- *Naturalis Historia* by Pliny the Elder, first century AD, in which the Latin author, at books XXXIV and XXXV describes some plant and animal colourants used for painting (Nat. Hist. XXXIV/XXXV).
- *De materia medica* by Pedanius Dioscorides, first century AD, in which the Greek author describes several plant and animal extracts (De materia medica).
- the *Leiden Papyrus* (Caley 1926) and the *Stockholm Papyrus* (Caley 1927), two collections of recipes datable to the third century AD, most probably written by the same unknown scribe.

As for Asian sources, Yu (1988) reviewed the extensive use of organic colourants described by ancient Chinese sources. According to these sources, since the sixth century AD vegetable and animal colourants were commonly used in combination with inorganic pigments. Examples were indigo laid under cinnabar in order to make the latter more purple; a mixture of vegetal and animal dyes called *rouge* in Chinese, made from lac dye, madder and safflower red, laid over cinnabar to make it redder; gamboge lightly applied over malachite to give it a more delicate shade of green.

Dyes, lakes and organic pigments in painting

Reds

Red dyes and lakes were widely used both for dyeing textile artworks and for painting. They were obtained by extraction from vegetal and animal sources; several recipes in ancient treatises well described the procedures to be applied (Phillipps 1847; Garzya Romano 1996). A secondary source for red dyes and lakes involved recycling the dyes used for textiles (Kirby et al. 2017): clippings of dyed cloth were subjected to extraction by boiling them in alkaline solutions, after which the addition of alum (potassium aluminium sulphate) would form a precipitate of $Al(OH)_3$ on which the textile dyes were absorbed. Although this procedure was commonly used from late Middle Ages, recent analytical evidence suggests that it could have been exploited already in Classical Antiquity (Dyer et al. 2018).

The use of red dyes on wall paintings must have been very common. In fact, a great number of identification of a generic "red lake" are present in the scientific literature, unfortunately without further specification. In most cases, the identification was obtained by polarised light microscopy (PLM) that allows distinguishing mineral red pigments from transparent or translucid dyes and lakes, or by UV light. Examples of generical identification of a red lake were in first century AD Nabatean wall paintings at Petra, Jordan (Akrawi and Shekede 2010), in eighth century Carolingian wall paintings at Müstair, Switzerland (Mairinger and Schreiner 1986; Cavallo et al. 2020), in eleventh to fourteenth century Tibetan-Buddhist wall paintings (Goepper et al. 1996; Skedzuhn et al. 2013; Yong and Shiwei 2014; Gill et al. 2014; Oeter and Skedzuhn-Safir 2015), in the Mogao caves in Dunhuang, China (AA.VV. 2013). Howard (2003) reported on numerous occurrences of red lakes in English medieval wall paintings and polychrome sculptures but she gave a precise identification of the dyes in three cases only. Identification of red lakes is common in polychrome clay figurines of the Hellenistic period also (Tsatsouli and Nikolaou 2017). Despite it is probable that most of this preliminary evidence could be attributed to madder lake, in particular when UV was used by the authors, further insights with more powerful techniques would be needed.

Red lakes were mostly used in wall paintings as glazes, due to their translucency, usually over a layer of lead white or of another pigment, mostly red. Their colour is not simply red but rather can encompass a large variety of hues, from dark purple to mauve, violet, red and pink. This is due to the fact that their preparation is largely dependent on the recipe used, which involves extraction from plants or insects followed by addition of chemical reagents, among which alum, lime, and gypsum. In alternative, they could be used mixed with blue pigments to obtain a purple hue.

One important drawback of red lakes is the fact that they are fugitive, that is they tend to fade under exposition to UV–visible light (Saunders and Kirby 1994), a feature that may have limited their use in wall paintings compared to the more stable cinnabar, red lead and red ochre. However, Howard (2003) reported a remarkable use of red lakes for large external polychromies on the portals and fronts of Amiens, Exeter and Lausanne Cathedrals.

Anthraquinones

The most important reds are anthraquinones and have a long history of exploitation as textile dyes, datable to at least the second millennium BC (Cardon 2007). The main members of the anthraquinone group are madder, extracted from the roots of plants of the *Rubiaceae* family, widespread all over the world, and the dyes extracted from scale insects, i.e. insects of the superfamily *Coccoidea*: kermes, from *Kermes vermilio*, widespread in the Mediterranean basin as well as in Iran and Iraq; Armenian cochineal, from *Porphyrophora hamelii*, characteristic of the countries of the Caucasian area such as Armenia and Azerbaijan; Polish cochineal, from *Porphyrophora polonica*, endemic to Eastern Europe; Mexican cochineal, from *Dactylopius coccus*, typical of South America; Indian lac or lac dye, from *Kerria lacca*, typical of India and Southeast Asia. The structures of the main molecules present in these dyes are shown in Fig. 1. The presence of anthraquinone red lakes on paintings can be identified in preliminary way by taking UV fluorescence images (Buzzegoli and Keller 2009) exploiting the characteristic emission. Then, further information can be obtained by means of high-performance liquid chromatography (HPLC), that allows to identify the biological source of the dye when specific chemical markers are identified.

Vegetal anthraquinones Madder was mainly extracted from the roots of *Rubia tinctorum*, a species widely diffused in the Mediterranean basin, but also from *Rubia peregrina* and *Rubia cordifolia* (Cardon 2007). The extraction was simple and consisted in treating bits of roots in boiling water in order to extract the molecules there contained. The extract was then filtered and could be used as such (this can be called *juice*) to impart delicate glazes on paintings, though relatively weak and fugitive. More frequently, it was added to alum and brought to alkaline pH in order to precipitate on aluminium hydroxide, or fixed on a white inorganic support such as white lead, calcium carbonate, gypsum, clays or earths, to produce *madder lake* (Daniels et al. 2014). The lake can be used like a pigment, though with less hiding power and chemical resistance.

A preliminary identification of madder in paintings can be obtained by exploiting the typical pinkish-orange fluorescence under UV irradiation. Using UV–visible diffuse reflectance spectrophotometry with optic fibres (FORS), madder shows two characteristic absorption bands occurring at ca. 510 and 540 nm (Aceto et al. 2014); alternatively, surface enhanced Raman scattering (SERS) analysis can be used for a fingerprint identification (Bruni et al. 2011).Then, an important insight is given by HPLC analysis, useful for recognising the specific vegetal species of origin: a high amount of alizarin typically addresses the source towards *Rubia tinctorum*, but high amounts of purpurin and the absence of alizarin (Mantzouris and Karapanagiotis 2015; Fostiridou et al. 2016; Dyer et al. 2018) address the source to *Rubia peregrina* or *Rubia cordifolia*. Cases are reported in diagnostic studies on Hellenistic and Roman artefacts in which madder lake markers were found together with markers of scale insect dyes (Mantzouris and Karapanagiotis 2015; Fostiridou et al. 2016; Andreotti et al. 2017; Dyer et al. 2018).

Madder lake was the most widely used red lake in wall paintings, possibly since it is the least fugitive among red dyes, and in the decoration of polychrome pottery (Bourgeois and Jeammet 2020), votive shards and stone artworks. The oldest reported occurrences on wall paintings date as far back as eighth century (see list in Table 1). Brecoulaki (2014) reports that madder lake was frequently used with Egyptian blue in paintings from the Bronze Age to

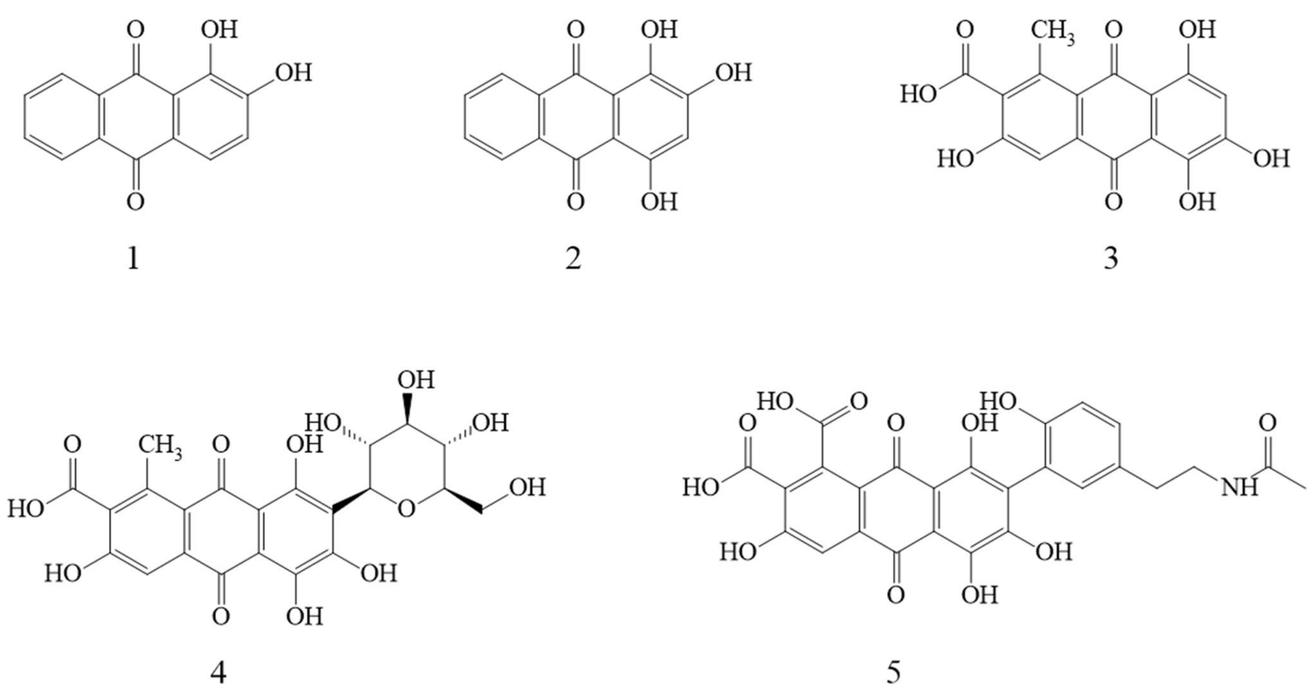

Fig. 1 Structures of the main molecules present in anthraquinone dyes: (1) alizarin (madder), (2) purpurin (madder), (3) kermesic acid (kermes), (4) carminic acid (Armenian cochineal, Mexican cochineal, Polish cochineal), (5) laccaic acid A (Indian lac)

Table 1 List of identification of madder in wall paintings

Date century	Provenance	Location	Object/samples	Technique[1]	Reference
8th–4th	Classical Greek	Corinth, Greece	Wall paintings	MALDI-ToF–MS	Sabatini et al. (2016)
7th BC	Egyptian	Kawa, Egypt	Wall paintings	PLM	Fulcher (2017)
6th–4th	Campanian	Cuma, Italy	Polychrome terracottas	HPLC–DAD	Bartolucci et al. (2007)
6th–2nd	Hellenistic	Koroneia cave, Greece	Painted *astragaloi*	HPLC–DAD	Colombini et al. (2004)
4th BC	Daunian	Ascoli Satriano, Apulia, Italy	Painted marble	HPLC–DAD	Giachi et al. (2009)
4th BC	Hellenistic	Tomb of Eurydice, Vergina, Greece	Painted marble	HPLC–DAD	Brecoulaki (2006)
4th BC	Hellenistic	Tomb of Persephone, Vergina, Greece	Wall paintings	HPLC–DAD	Brecoulaki (2006)
4th BC	Hellenistic	Tomb of Aienia III, Nea Michaniona, Greece	Wall paintings	HPLC–DAD	Brecoulaki (2006)
4th BC	Hellenistic	Tomb of Potidea, Greece	Painted marble	HPLC–DAD	Brecoulaki (2006)
4th BC	Hellenistic	Tomb of Aghios Athanasios, Greece	Wall paintings	HPLC–DAD	Brecoulaki (2006)
4rd–3nd	Hellenistic	Grand tumulus, Vergina, Greece	Painted marble	HPLC–DAD	Brecoulaki (2006)
4rd–3nd	Hellenistic	Tomb of the Palmettes, Lefkadia, Greece	Wall paintings	HPLC–DAD	Brecoulaki (2006)
4rd-3nd	Hellenistic	Greece	Polychrome terracottas	PP	Pagès-Camagna (2010)
4rd–3nd	Daunian	Ascoli Satriano, Apulia, Italy	Marble basin	FS	Wallert (1995)
4th–3rd	Hellenistic	Cristallini tomb, Naples	Wall paintings	HPLC–DAD	Andreotti et al. 2017)
4th–2nd	Hellenistic	Delos, Greece	Wall paintings	MALDI-ToF–MS	Sabatini et al. (2016)
4th–2nd	Hellenistic	Amphipolis, Greece	Stone funerary monument	PP	Brecoulaki et al. (2006)
3rd BC	Etruscan	Museo ArcheologicoRegionale, Palermo, Italy	Alabaster sarcophagus		Gagliano Candela et al. (2019)
3rd BC	Hellenistic	Canosa di Puglia, Italy	Polychrome terracottas	PP	Kakoulli et al. 2017)
3rd BC	Hellenistic	Canosa di Puglia, Italy	Polychrome terracottas	HPLC–MS	Dyer et al. (2018)
3rd–2nd	Hellenistic	Taranto, Italy	Painting on clay vessel	MALDI-ToF–MS	Sabatini et al. (2016)
3rd–2nd	Hellenistic	Thessaloniki, Greece	Polychrome terracottas	HPLC–DAD	Mantzouris and Karapanagiotis (2015)
3rd–2nd	Hellenistic	Thessaloniki, Greece	Polychrome terracottas	HPLC–DAD	Fostiridou et al. (2016)
1st BC	Hellenistic	Myrina, Turkey	Polychrome terracottas	PILI	Dyer and Sotiropoulou (2017)
1st AD	Roman	Villa San Marco, Stabiae	Wall paintings	RS	Guichard and Guineau (2002)
1st AD	Roman	Domus Aurea, Rome	Wall paintings	FS	Clementi et al. (2011)
1st AD	Roman	Terme degli Stucchi Dipinti, Rome	Painted fragments	GC–MS	Gismondi et al. (2018)
1st AD	Roman	Pompeii	Pigments	SERS	Marcaida et al. (2018)
1st–2nd	Parthian	Uruk, Iraq	Painted stuccoes	HPLC–DAD	Simpson et al. (2012)
2nd AD	Roman	Hierapolis, Turkey	Painted sculptures	HPLC–DAD	Bracci et al. (2019)
2nd AD	Greek	Korinthos, Greece	Wall paintings	HPLC–DAD	Karapanagiotis and Chryssoulakis (2006)
Roman age	Roman	Vaison-la-Romaine	Wall paintings	RS	Guichard and Guineau (2002)
12th AD	Persian	Mount Sofeh in Isfahan, Iran	Wall paintings	HPLC–MS	Holakooei et al. (2020)
13th–14th	English	Ante-Reliquiary Chapel, Norwich	Wall paintings	FS	Howard (2003)
14th AD	English	St. Albans Cathedral	Polychrome statue	DT-MS	Howard (2003)
14th–15th	Indo-Tibetan	Saspol caves, Ladakh	Wall paintings	IRFC	Pinto et al. (2018)
16th AD	Portuguese	Convent of Christ, Tomar, Portugal	Wall paintings	HPLC–MS	Manhita et al. (2016)

[1] *DT-MS*, direct temperature resolved mass spectrometry; *FS*, fluorescence spectroscopy; *GC–MS*, gas chromatography–mass spectrometry; *HPLC–DAD*, high-performance liquid chromatography–diode array detector; *HPLC–MS*, high-performance liquid chromatography–mass spectrometry; *IRFC*, infrared false colour; *MALDI-ToF–MS*, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry; *PILI*, photo-induced luminescence imaging; *PLM*, polarised light microscopy; *PP*, photoluminescence photography; *RS*, reflectance spectrophotom-

Table 1 (continued)

etry; *SERS*, surface enhanced Raman scattering.

Hellenistic times, either in mixture or in superimposed layers; the same was reported by Guichard and Guineau on Roman age paintings (2002).

A list of identification is reported in Table 1.

In one case, a pink-purple pigment found in Pompeii (Clarke et al. 2005), madder was identified together with ellagic acid, a chemical marker of hydrolysable tannins used in the dyeing of textiles: these evidences suggest that the lakes were prepared from clippings of dyed cloth, a practice commonly reported for medieval lakes but rarely reported for Hellenistic-Roman times.

It is interesting to note that most of the diagnostic studies on ancient paintings report the predominant, if not exclusive, presence of purpurin in place of alizarin, a chemical composition very different from that recorded in the madder lakes used in later western European canvas paintings. It is possible that this difference be related to different methods of preparation of the lakes, but more probably it reflects the use of a different plant source, i.e. *Rubia peregrina* rather than *Rubia tinctorum*.

Animal anthraquinones Dyes and lakes from scale insects were considerably more expensive than madder, at least according to the medieval and Renaissance literary sources available. Pharmacy price lists in fifteenth to sixteenth century Germany (Burmester and Krekel 1998) suggest that madder was even 40 times cheaper than *grana*, the name with which kermes was indicated in Italian medieval treatises. Similarly lac dye or Indian lac, the red dye extracted from the scale insect *Kerria lacca*, native to India and south-eastern Asia, was considered as an exceptionally expensive material, inferior in price only to gold and ultramarine (Kirby 2000; Howard 2003). The use of such lakes on wall paintings must be always regarded as symptom of high-quality commissions. Therefore, it is not surprising that the number of identification of lakes from scale insects be lower than for madder.

The identification of scale insect dyes and lakes is not easy in a non-invasive way. Using FORS, scale insect dyes show two characteristic absorption bands occurring at slightly longer wavelengths than in madder (Aceto et al. 2014). It is not possible, however, distinguishing the various scale insect dyes among themselves on the basis of FORS features; this requests micro-invasive techniques, such as SERS (Bruni et al. 2011) or HPLC (Shahid et al. 2019) by detection of the chemical markers specific for each dye.

Howard et al. (2020) reported only two occurrences of kermes in English medieval wall paintings: in the fourteenth century scheme in the chapter house of Westminster Abbey in London, most probably a sign of the importance of the Westminster paintings, and over the late fourteenth century tomb of the Black Prince in Canterbury Cathedral, in this case along with lac dye and madder. Highly remarkable evidences of kermes were recently given by Osticioli et al. (2019) who identified the lake in one of the most famous wall paintings, Leonardo da Vinci's *Last Supper*, kept in Santa Maria delle Grazie church in Milan, and in Masolino da Panicale's *Beheading of St. John the Baptist*, kept in the baptistery of in Castiglione Olona (Varese, Lombardy), both datable to fifteenth century; the analytical technique used was Subtracted Shifted Raman Spectroscopy (SSRS).

Two other scale insect dyes are Armenian cochineal from *Porphyrophora hamelii*, and Polish cochineal from *Porphyrophora polonica*. They were widely used in textile dyeing in Europe and Central Asia, but in painting the evidence is at present few. A single identification is known: in a collection of Hellenistic terracotta funeral figurines found in Thessaloniki (Macedonia, Greece), datable to third to second century BC, HPLC–DAD analysis on samples from pink lakes identified the presence of carminic acid, marker for cochineal; the absence of kermesic and flavokermesic acid, markers for Polish cochineal, suggested that Armenian cochineal was the dye used for the preparation of the lakes (Mantzouris and Karapanagiotis 2015; Fostiridou et al. 2016); the scale insect dye was found together with purpurin, possibly originating from *Rubia peregrina* or *Rubia cordifolia*.

Mexican cochineal, the dyestuff extracted from *Dactylopius coccus*, has a long history of use in South America (Cardon 2007). After the conquest of Mexico by Hernan Cortés in 1521, cochineal was exported in Spain and then to the rest of Europe and Asia and soon became highly appreciated, becoming the second-most profitable trade item from the New World after silver (Anderson 2015). This was due to the high content of dye in the insects' body, estimated at 10 times than that contained in the European and Asian species. In South America, while the lake appears to have been frequently used in manuscripts and documents, its presence is only suggested in wall paintings from the Maya and Zapotec sites (Brittenham 2015). Magaloni-Kerpel attributed to Mexican cochineal (although without analytical evidence),

Table 2 List of identification of lac dye in wall paintings

Species[1]	Date	Provenance	Location	Object/samples	Technique[2]	Reference
Ac	3^{rd}–2^{nd}	Hellenistic	Thessaloniki, Greece	Polychrome terracottas	HPLC–DAD	Fostiridou et al. (2016)
Ke	14^{th} AD	English	Westminster Abbey, London	Wall paintings	HPLC–DAD	Howard et al. (2020)
Ke	14^{th} AD	English	Canterbury Cathedral	Stone sculpture	HPLC–DAD	Howard et al. (2020)
Ke	14^{th} AD	English	British Musem, London	Alabaster panels	HPLC–MS	Pereira-Pardo et al. (2019)
Ke	15^{th} AD	Italian	*The Last Supper*, Leonardo da Vinci	Wall paintings	Raman	Osticioli et al. (2019)
Ke	15^{th} AD	Italian	*The Beheading of St. John the Baptist in the Baptistery*, Masolino da Panicale	Wall paintings	Raman	Osticioli et al. (2019)
Ld	3^{rd} BC	Greek	Canosa di Puglia, Italy	Polychrome terracottas	HPLC–MS	Dyer et al. (2018)
Ld	5^{th}–7^{th}	Buddhist	Kizil Grottoes, China	Wall paintings	HPLC–MS	Zhou et al. (2020)
Ld	9^{th}–10^{th}	Chinese	Mogao caves in Dunhuang, China	Wall paintings	HPLC–MS	AA.VV. (2013)
Ld	11^{th}–12^{th}	Tibetan	Nako Monastery, Northern India	Wall paintings	HPLC–DAD	Bayerová (2018)
Ld	13^{th}–14^{th}	English	Westminster Abbey, London	Wall paintings	HPLC–DAD	Howe (2006)
Ld	14^{th} AD	English	Westminster Palace, London	Painted fragments	HPLC–DAD	Howard et al. (2020)
Mc	2^{nd} BC–8^{th} AD	Zapotecs	Oaxaca, Mexico	Wall paintings	undefined	Magaloni-Kerpel (2010)
Mc	3^{rd}–9^{th}	Maya	Náprstek Museum in Prague	Polychrome terracottas	FT-IR	Klouzkova et al. (2018)
Mc	16^{th}–17^{th}	Spanish	Augustinian ex-convents in Mexico	Wall paintings	Raman	Ruvalcaba-Sil et al. (2017)
Mc	17^{th}–18^{th}	Spanish	Colonial missions, Chihuahua, Mexico	Wall paintings	FORS	Casanova-González et al. (2020)
Mc	18^{th} AD	Andean	San Andrés de Pachama, Chile	Wall paintings	HPLC–DAD	Tomasini et al. (2018)

[1] *Ac*, Armenian cochineal; *Ke*, Kermes; *Ld*, lac dye; *Mc*, Mexican cochineal; *Pc*, Polish cochineal.

[2] *FT-IR*, infrared spectrophotometry; *HPLC–DAD*, high-performance liquid chromatography–diode array detector; *HPLC–MS*, high performance liquid chromatography–mass spectrometry; *Raman*, Raman spectroscopy.

the organic lakes found in the paintings of some Zapotecs tombs in the Central Valleys of Oaxaca, Mexico, datable between 200 BC and 800 AD; the lakes were mixed with hematite or with hematite and cinnabar to make what has been called "Zapotec Red" for the backgrounds of scenes of funerary rituals (Magaloni-Kerpel 2010). Further investigation is of course needed to understand the real extension of the use. In the European textile dyeing sector, cochineal quickly replaced the other species, but it is hard to evaluate how such phenomenon occurred in European painting, due to the low number of precise identification; the lake has been identified in canvas paintings (Anderson 2015), but no case are reported in wall paintings.

Slightly higher is the number of identification of Indian lac or lac dye, the red dye extracted from *Kerria lacca*, a scale insect species typical of India and Southeast Asia. Among the anthraquinone dyes extracted from scale insects, lac dye must have been particularly appreciated; this would explain the fact that it was imported in the Mediterranean basin from the very distant India already in the Hellenistic period.

A list of identification of the main scale insect dyes and lakes is reported in Table 2.

A remarkable case is the purple pigment found on third century BC terracotta oinochoes from Canosa di Puglia, southern Italy (Dyer et al. 2018) in which the authors reported the contextual identification of lac dye, of purpurin (marker for a dye extracted from a plant of the *Rubiaceae* family) and of ellagic acid (indicative of hydrolysable tannins used in the dyeing of textiles): this is one of the earliest evidence of the production of organic lakes from clippings of dyed cloth. Zhou et al. (2020) recently reported on the use of lac dye as mordant for adhering gold foils in the wall paintings of Kizil Grottoes, north-western China, datable between fifth and seventh century AD.

Brazilwood

Apart from the anthraquinone dyes, there are many other red dyes, mostly of vegetal origin. All of them, however, have been rarely used on wall paintings. Brazilwood is extracted from the bark of *Caesalpinia sappan* L., a plant typical of South-east Asia imported in Europe from the tenth century, or of *Caesalpinia echinata* and *Haematoxylum brasiletto*, South American species imported in

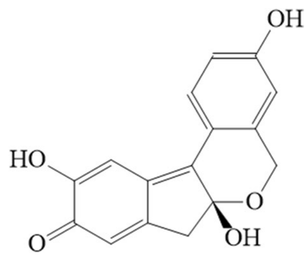

Fig. 2 Structure of brasilein, the main molecule present in brazilwood

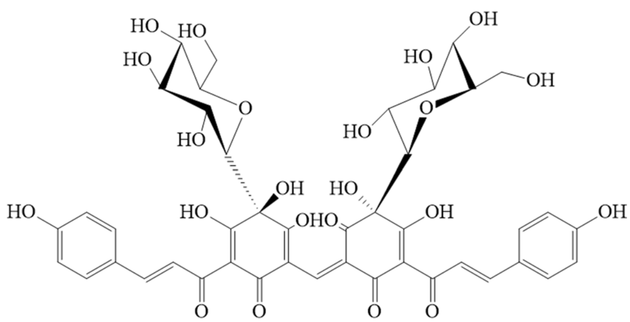

Fig. 3 Structure of carthamin, the main molecule present in safflower red

Europe from the sixteenth century. It was widely used in textile dyeing (Cardon 2007) and in miniature painting (Vitorino et al. 2016), in particular in Late Middle Ages and Renaissance Europe. The structure of brasilein, the main molecules of brazilwood, is shown in Fig. 2. The identification of brazilwood is possible by means of FORS (Aceto et al. 2014), spectrofluorimetry (Melo et al. 2014) or SERS (Bruni et al. 2011). However, possibly due to the fact that it was considered the most fugitive among red dyes, the use of brazilwood in wall paintings has been demonstrated only two times (Howard 2003): in the fourteenth century choir screens at Cologne Cathedral and in the already cited fourteenth century paintings in the chapter house of Westminster Abbey in London, where it was found mixed with kermes, possibly as a consequence of the use of lakes extracted from a dyebath of cloth clippings.

Safflower red

Safflower red is one of the two colourants extractable in water from the *Carthamus tinctorius* plant. While safflower yellow (C.I. Natural Yellow 5) is extracted at neutral pH, safflower red (C.I. Natural Red 26) is extracted at alkaline pH. Both were used as textile dyes since ancient times (Cardon 2007). The structure of carthamin, the main molecule present in safflower red, is shown in Fig. 3. The identification of safflower yellow and red is possible by means of HPLC (Wouters et al. 2010) or SERS (Bruni et al. 2011). Their use in wall paintings, and in overall painting art, is however uncertain since they have never been identified on such artworks up to now. Wouters et al. (2010, 2011a, b) verified the possibility of preparing safflower pigments by following ancient Chinese texts, and produced reference samples. Documents found in the famous caves of Mogao (Gansu province, China) attest the use of safflower red according to donors offering the colourant for decorating the caves (Shekede et al. 2010)..

Yellows

Despite the availability of several yellow dyes used in textile art and handed down to canvas and miniature painting, such as saffron, weld, and turmeric, very few of them are suitable for wall painting for the reasons previously detailed by Cennino Cennini. In the Mediterranean world, yellow organic colourants have been rarely identified. Considering the most important class of yellow dyes as far as textile dyeing is concerned, that is the flavonoids, there is one case reported in the scientific literature: in the Roman necropolis of Carmona, Sevilla (Spain), datable from the first century BC to the second century AD, in a recent study on the wall paintings (Jorge-Villar et al. 2018), the authors identified weld, the dye extracted from the *Reseda luteola* plant, in admixture with blue for obtaining a green colour, as suggested by Vitruvius (De Architectura VII, 14, 2). Akrawi and Shekede (2010) reported a generic "yellow organic matrix" in their study of first century Nabatean wall paintings at Petra (Jordan). It must be considered, however, that the identification of yellow dyes is more difficult than that of red dyes using non-invasive techniques. The spectral features of the different dyes in FORS analysis are not specific enough (Aceto et al. 2014). Therefore, micro-invasive techniques are generally needed. SERS (Bruni et al. 2011) and HPLC (Lech 2020) provide the best diagnostic power for a selective identification.

However, if we look beyond Europe, some solutions also appear for this colour area. In the ninth to tenth century AD wall paintings at Mogao Cave 85 in Dunhuang (China) where traces of genistein found by means of HPLC–MS suggested an original presence of a yellow flavonoid dye, now probably faded (AA.VV. 2013); the authors of the study suggested that one possible vegetal source could be the Asian orange-dye-yielding plant *Flemingia macrophylla*.

Indian yellow

An organic pigment with a very peculiar story is *Indian yellow*: originally introduced in India from Persia in fifteenth century AD (Ploeger and Shugar 2017), it was produced from the urine of cows fed only with mango leaves, a practice that generated a powdery pigment with a beautiful yellow colour

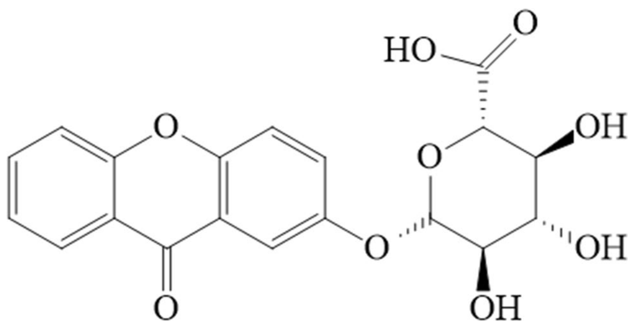

Fig. 4 Structure of euxanthic acid, the main molecule present in Indian yellow

but also condemned cows to starvation. This made the producers of the pigment quite unpopular among Hindi people, so that the whole production was prohibited in 1908 (Baer et al. 1986). The composition of Indian yellow has long been part of a mystery. According to many literary sources of the past, it was unclear whether its origin was vegetal or animal (Ploeger and Shugar 2017 and references therein); in addition, on the colour market, it was frequently adulterated or substituted with cheaper pigments such as chrome yellow, tartrazine or cobalt yellow. It is now consolidated the fact that true Indian yellow is a mixture of Ca^{2+} and Mg^{2+} salts of euxanthic acid (structure in Fig. 4) and of other compounds, among which euxanthone (Tamburini et al. 2018). Indian yellow was used mainly for watercolour and tempera-like paints, and therefore its main application was in miniature painting, but since it was found to be resistant to alkali (Field 1809), its use in fresco painting was suggested. The identification of Indian yellow can be obtained by means of Raman spectroscopy (de Faria et al. 2017) or HPLC–MS (Tamburini et al. 2018). At present, however, only two cases of identification in wall paintings are reported: the seventeenth century paintings within the Garh Palace in Bundi, Rajasthan (India) (Tamburini et al. 2018) and paintings datable between fifteenth and eighteenth century in a church in the Skopje Fortress (Macedonia) (Tanevska et al. 2009).

Gamboge

Another yellow vegetal dye is *gamboge*, extracted from the latex of trees of *Garcinia* genus, indigenous to south-eastern Asia. This colourant, which is composed by structure is shown in Fig. 5, was frequently used in far eastern Asian painting schools, but its occurrence in wall paintings has been evidenced only once, in a yellow glaze identified by means of Raman spectroscopy and HPLC–DAD in eleventh to twelfth century AD Buddhist wall paintings at Nako Monastery, in northern India (Bayerová 2018). Due to the relative difficulty in its identification, it is possible that it had been used in other unreported instances, however. Riederer (1977) tentatively hypothesised the use of gamboge, kermes and madder lake for Late Antique and early medieval Asian wall paintings, kept at the Asian Art Museum in Berlin.

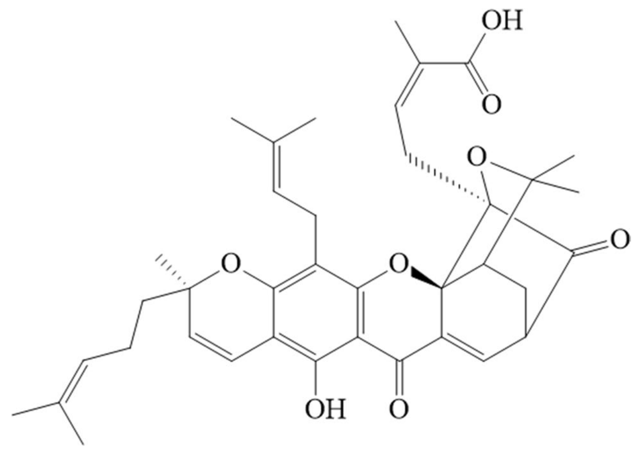

Fig. 5 Structure of gambogic acid, the main molecule present in gamboge

Greens

The use of organic greens on wall paintings has been quite limited. The few available green dyes (*iris* from the petals of *Iris germanica*, *sap green* from the ripe berries of *Rhamnus cathartica* L.) were so poorly reliable that dyers themselves, to dye in green, referred using double dyeing with indigo and a yellow dye rather using green dyes. Two green colourants of partial organic nature can be included in the discussion: *verdigris* and *copper resinate*.

Verdigris

A partially organic pigment is *verdigris*, an umbrella term for a complex mixture of hydrated Cu^{2+} acetates with different hydration and basicity degrees, as well as slightly different colours. The following compounds are reported (Chaplin et al. 2006; San Andrés et al. 2010): $Cu(CH_3COO)_2·H_2O$, $[Cu(CH_3COO)_2]·2[Cu(OH)_2]$, $Cu(CH_3COO)_2·3Cu(OH)_2·2H_2O$ $[Cu(CH_3COO)_2]·Cu(OH)_2·5H_2O$, $[Cu(CH_3COO)_2]_2·Cu(OH)_2·5H_2O$, and $[Cu(CH_3COO)_2]_2·Cu(OH)_2·5H_2O$. This variability is a consequence of the variations in the recipes which basically refer to the action of vinegar on copper but can include wine making by-products, soap, honey, sodium or ammonium chloride, and urine. Copper can be exposed to vinegar vapours or directly immersed into vinegar; moreover, the exposure time can vary from 15 days to 6 months. Among the green colourants used in painting, verdigris is one of the most important. In miniature painting, it was the most commonly used since early Middle Ages. Even before, it was mentioned by Theophrastus, Dioscorides and Pliny the Elder. Pliny, in particular (Nat. Hist. XXXIV, 26), wrote about the frequent use of *aerugo* (verdigris) and detailed the various passages of its production. From his chronicle, we can guess that in Roman times it was a valuable pigment, since he also stated that it was often falsified. The identification of verdigris can be obtained by means of Raman spectroscopy (San Andrés et al. 2010). Despite ancient literary evidence, the occurrence of verdigris in wall paintings of Greek-Roman age has been rarely reported and never as the main green pigment. Kakoulli (2002) in her survey on Late classical and Hellenistic paintings artworks, did not report verdigris in any instance. Villar and Edwards (2005) analysed samples from several paintings excavated in first century BC to first century AD Roman villas in Burgos (Spain) but identified the pigment in a single instance. A more frequent use is instead reported in the Middle Ages. Cennino Cennini, in chapter LXXII of his *Il libro dell'arte* treatise, warned not to use *verderame* (verdigris) in the *buon fresco* painting technique, which is consistent with the instability of the pigment in lime; he does not, however, warn against its full use in wall painting. Damiani et al. (2014) identified verdigris in the dark green areas on the fourteenth century *Madonna and Child enthroned with Saints* wall painting of Ambrogio Lorenzetti, kept inside St. Augustine church in Siena, Italy. Fioretti et al. (2020) recently identified verdigris mixed with green earth in the fifteenth century paintings at S.ta Maria Veterana, near Bari (Apulia, Italy). Howard (2003) reported several cases of the use of verdigris in Gothic wall paintings in England, as well as in polychrome sculpture artworks, together with accounts for the purchase of the pigment that in late medieval England seemed to be cheap and readily available. Another evidence of the use of verdigris in the context of medieval England was in the polychromy of a fourteenth century alabaster statue kept in the British Museum collection (Pereira-Pardo et al. 2019). Rollier-Hanselmann (1997) cited the identification of verdigris in Romanesque wall paintings in France, as well as in early medieval wall. Verdigris was found applied with oil painting and mostly mixed with lead white in all cases detected, coherently with the suggestion of Cennino Cennini.

Copper resinate

Another partially organic green pigment, and an umbrella term as well, is copper resinate. It is a synthetic colourant obtained by boiling a copper salt, usually verdigris, with different organic ingredients, among which Venice turpentine, colophony, pine resin, or mastic, characterised by a high content in terpenic compounds, but also siccative oils. The resulting product is a translucid green pigment with low hiding power, useful for glazes. It was produced since the eighth century and it is reported to be used, at least on canvas painting, up to the seventeenth century, but its poor resistance to fading was at any rate well known to artists. The identification of copper resinate is complicated by the fact that it is not easy to understand the role of verdigris in the preparation; Raman spectroscopy can be used (Conti et al. 2014) but confirmation must be given by detection of the resinous compounds involved. The features of copper resinate are particularly unsuitable for wall paintings, and not surprisingly up to know it has been evidenced in very few instances: in thirteenth to fourteenth century wall paintings in San Juan del Hospital Church in Valencia (Spain), made by an anonymous artist (Doménech-Carbó et al. 2000), in the twelfth century Romanesque portal of the abbey-church of Cluny, where Castandet and Rollier-Hanselmann (2013) tentatively identified copper resinate mixed with lead–tin yellow in some green areas, and in the previously cited polychromy of a fourteenth century alabaster statue kept in the British Musem collection (Pereira-Pardo et al. 2019) where the pigment could have been used to impart a glossy effect to the underlying alabaster substrate and to gilded areas. Again, Howard (2003) reported that some studies have suggested the presence of copper resinate in medieval wall paintings and polychrome sculpture artworks according to the contextual identification of copper and resinous compounds, but the author correctly advised against the possibility that such evidence could be related to resins simply added to verdigris (but not after reaction with) in order to improve the glazing properties of the green paint.

Purple

Since Antiquity, the purple colour has been always considered as synonymous of power and richness. This can be partially (but not entirely) explained with the high cost of production of the purple pigment *par excellence*, the famous *Tyrian purple* obtained from mollusks of the *Murex* genus, also considering that no other pure colourants were available for painting in purple.

The only member of this group is therefore *Tyrian purple*, the famous colourant produced from the hypobranchial gland of various shellfish species of *Murex* genus. The structures of the main molecules present in Tyrian purple, as well as those present in indigo and woad (see later) are shown in Fig. 6. Despite its role in the history of Mankind is mainly connected with the dyeing of precious garments produced for kings, emperors and high ecclesiastical offices (Karapanagiotis 2019), Tyrian purple was used for painting and in particular in wall paintings, being insoluble in water and therefore suitable as a pigment. Its colour is characteristic but, as in the case of red dyes, different recipes—and different shellfish species as well—can yield slightly different hues. However, very few analytical evidences of its real presence have been given, while in many more instances it was

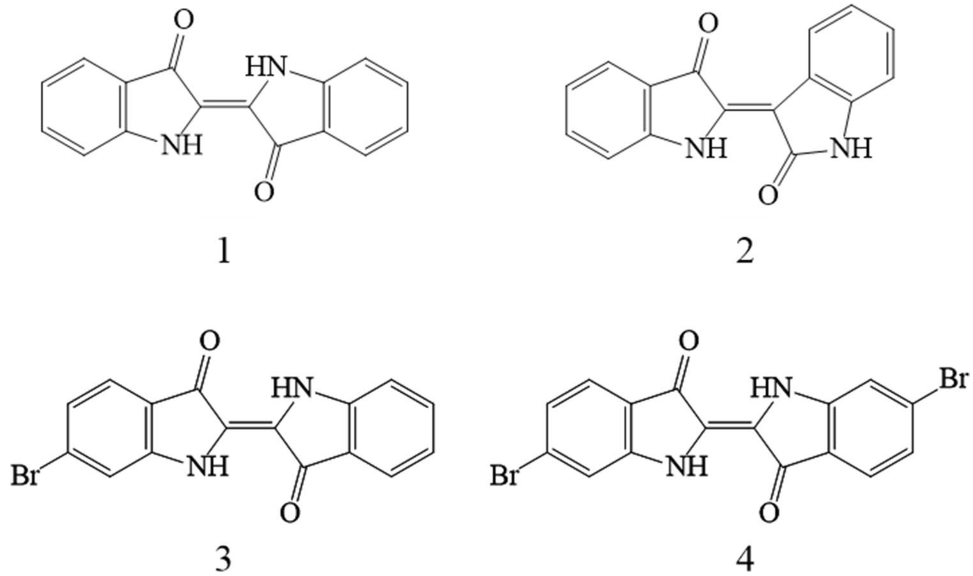

Fig. 6 Structures of the indigoid molecules present in Tyrian purple, indigo and woad: (1) indigotine (indigo/woad and Tyrian purple), (2) indirubine (indigo/woad and Tyrian purple), (3) 6-monobromoindigotine (Tyrian purple), (4) 6,6′-dibromoindigotine (Tyrian purple)

found that cheaper substitutes, such as mixtures of madder and Egyptian blue or indigo, were used instead (Brecoulaki 2014; Dyer and Sotiropoulou 2017).

Pliny the Elder described (Nat. Hist. XXXV, 26) the method of preparation of *purpurissum*, the pigment obtained from shellfish. According to his description, the preparation of the pigment could occur in the same bath used for dyeing textiles, and therefore in the same context of the dyeing industry. Pliny tells that *creta argentaria* was to be added to absorb the colour from the bath; based on diagnostic evidence this can be identified with chalk in the form of aragonite (Karapanagiotis et al. 2017) or kaolinite (Papliaka et al. 2017). Readers should not be misled by this addition: it was not done in order to obtain a true lake as defined in chapter 2, but rather for the need of tuning the purple hue of the pigment (Boesken Kanold 2011).

The identification of Tyrian purple, as well as that of indigo (see below) is relatively easier than that of all other dyes. Its behaviour as a pigment facilitates the visualisation of the particles and more generally the response to the various diagnostic techniques. FORS analysis can provide a preliminary identification according to a characteristic absorption bands occurring at ca. 525 nm (Aceto et al. 2014). Elemental analysis can provide an indirect identification through the presence of two bromine atoms in the structure of 6,6′-dibromoindigotine, a feature exploited in several instances (Aloupi et al. 2000; Maravelaki-Kalaitzaki and Kallithrakas-Kontos 2003; Sotiropoulou 2004; Coccato et al. 2020); care must be taken, however, as a recent work (Aceto et al. 2015) demonstrated that the sole evidence of bromine is not enough for an exclusive identification of Tyrian purple: other dyes such as orchil and folium can have significant amounts of bromine. Raman spectroscopy (Karapanayiotis et al. 2004) can provide a fingerprint identification without the need of exploiting the SERS method, a feature almost unique among organic colourants. Finally, HPLC can be used in order to trace the animal source by the distribution of the chemical compounds (Karapanagiotis 2019).

The number of identification of Tyrian purple on wall paintings and other painted artworks on inorganic supports is limited, as evidenced by the recent review by Karapanagiotis (2019). An updated list is reported in Table 3.

The oldest evidence of the use of Tyrian purple as a pigment is related to the Minoan civilisation. It is dated to eighteenth to seventeenth century BC and refers to the islands of Santorini and Rhodes in the Aegean Sea. According to these findings, the Minoans developed the use of this colourant, both for painting and for dyeing, well before the Phoenicians. Most of the identification is in painted artworks of the Late Bronze Age to Hellenistic times; Brecoulaki (2014) cites the frequent use of mixtures, or superimpositions, of Tyrian purple with Egyptian blue, as well as in the case of madder. The precious pigment was used for painted artworks of particular value and/or in selected figurative motifs in order to emphasise the symbolic value of the composition. One remarkable example is the purple applied on the crocus petals of the *Saffron Gatherers* depiction at Akrotiri, on the island of Thera, nowadays Santorini (Sotiropoulou 2004). Another example is the particular hue obtained by mixing Tyrian purple with Egyptian blue to depict the sea in the Naval Scene painting at the Palace of Nestor at Pylos, a Mycenaean site, datable to 1200 BC (Kokiasmenou et al. 2020). Later on, the current archaeological records indicate the predominant use in the eastern Mediterranean basin up to first century BC, with a single evidence reported for the entire Middle Ages, referring to the twelfth century paintings in the Church of Sainte Madeleine at Manas, Department of Drôme, south-eastern

Table 3 List of identification of Tyrian purple in wall paintings

Date	Provenance	Location	Object/samples	Technique[1]	Reference
18^{th}–17^{th}	Minoan	Akrotiri, Thera, Greece	Wall paintings	HPLC–DAD	Sotiropoulou (2004)
18^{th}–17^{th}	Minoan	Raos, Thera, Greece	Wall paintings	HPLC–DAD	Karapanagiotis et al. (2013)
17^{th} BC	Minoan	Akrotiri, Thera, Greece	Purple pigment	Raman	Van Elslande et al. (2008)
17^{th} BC	Minoan	Trianda, Rhodes, Greece	Purple pigment	HPLC–DAD	Karapanagiotis et al. (2013)
13^{th} BC	Mycenean	Nestor Palace, Peloponnese, Greece	Wall paintings	XRF	Kokiasmenou et al. (2020)
6^{th}–2^{nd}	Hellenistic	Koroneia cave, Greece	Painted *astragaloi*	HPLC–DAD	Colombini et al. (2004)
5^{th} BC	Persian	Daskyleion, Turkey	Burial kline	HPLC–DAD	Papliaka et al. (2017)
4^{th} BC	Hellenistic	J. Paul Getty Museum, California	Marble vessel	XRF	Dennis et al. (2001)
4^{th} BC	Hellenistic	Tomb of Aghios Athanasios, Greece	Wall paintings	HPLC–DAD	Brecoulaki (2014)
4^{th} BC	Etruscan	Amazon Sarcophagus, Tarquinia, Italy	Painted stone	HPLC–DAD	Giachi et al. (2007)
4^{th} BC	Etruscan	Tomb of Reliefs, Cerveteri, Italy	Wall paintings	Raman	Alfeld et al. (2019)
4^{rd}–3^{nd}	Hellenistic	Tomb of the Palmettes, Lefkadia, Greece	Wall paintings	HPLC–DAD	Brecoulaki (2006)
4^{th}–3^{rd} *	Daunian	Sansone Collection, Italy	Ceramics	IR	Antonacci Sanpaolo et al. (1990)
4^{th}–2^{nd}	Hellenistic	Delos Museum, Greece	Purple pigment	XRF	Karydas et al. (2009)
4^{th}–2^{nd}	Hellenistic	Tomb of Philosophers, Pella, Greece	Wall paintings	SEM–EDX	Maniatis et al. (2007)
3^{rd} BC	Hellenistic	Crete, Greece	Polychrome terracottas	HPLC–DAD	Maravelaki-Kalaitzaki and Kallithrakas-Kontos (2003)
3^{rd} BC	Hellenistic	Tomb of the Palmettes, Lefkadia, Greece	Wall paintings	HPLC–DAD	Brecoulaki (2010)
1^{st} BC	Persian	Bible Lands Museum, Jerusalem	Marble vessel	HPLC–DAD	Koren (2008)
1^{st} AD	Roman	Pompeii, Italy	Purple pigment	HPLC–DAD	Clarke et al. (2005)
1^{st}–2^{nd}	Roman	Lateran area, Rome	Painted plasters	XRF	Coccato et al. (2020)
12^{th} AD	French	Church of Sainte Madeleine, Manas, France	Wall paintings	HPLC–MS	March et al. (2011)

[1]*GC-MS*, gas chromatography–mass spectrometry; *HPLC–MS*, high-performance liquid chromatography–mass spectrometry; *IR*, infrared spectroscopy; *IRFC*, infrared false colour; *PLM*, polarised light microscopy; *Raman*, Raman spectroscopy; *SEM–EDX*, scanning electron microscopy–energy dispersive X-ray; *XRF*, X-ray fluorescence spectrometry.

France (March et al. 2011), interestingly a church linked with the Knights Templar.

It is possible that, as a consequence of an increase in diagnostic studies, further evidence may be brought to light in order to extend the period and the geographic areas of use. It is in fact necessary to make a consideration, from a logistical point of view based on the possibility that the production of the pigment was closely linked with the production of the textile dye, as it is suggested in recent studies (Sotiropoulou et al. 2021): the number of sites that show archaeological evidence of the purple dye industry is currently very high (Kalaitzaki et al. 2017; Marín-Aguilera et al. 2019) and this suggests that the contextual production of the pigment, and therefore its use in painting, may/must have been much greater than what has been highlighted so far by diagnostics.

To overcome the high cost of Tyrian purple, artists often sought alternative solutions for the purple colour in their artworks. It was reported by some chroniclers of the Greek-Roman era, among which Pliny the Elder, Theophrastus and Vitruvius, that cheaper substitutes of Tyrian purple were used in ancient times, both in textile industry and in painting. Vitruvius (De. Arch. VII, 14), tells about a purple colour obtained by mixing chalk with madder or with *hysginum*, this last attributed to kermes or other dyes extracted from scale insects. Dyes extracted from lichens are cited as substitutes (Aceto et al. 2015). A confirmation can come from the identification of orchil, the dye extracted from *Roccella tinctoria* and other lichen species, in the polychromies of the collection of Greek terracotta figurines in the Musée du Louvre (Pagès-Camagna 2010). Brecoulaki suggested that the purple floral motifs and the garments painted on three marble pyxides kept at the National Archaeological Museum of Athens, datable to the end of fifth century BC, could be rendered with orchil (Brecoulaki et al. 2014), due to the lack of analytical evidence for Tyrian purple or even madder. Pereira-Pardo et al. (2016) in their study on sixteenth century wall paintings from Ribeira Sacra (Galicia, north-western Spain), detected a purple colourant of organic nature, tentatively attributed to orchil or to an extract from vine grape (*Vitis vinifera*) but no analytical evidence was given.

Blues

The use of organic blue colourants in wall paintings is later than the other colours, despite the fact that indigo and woad were available for dyeing and painting since at least the second millennium BC (Cardon 2007).

Indigo and woad

A remarkable blue organic colourant is *indigo*, extracted from the leaves of *Indigofera tinctoria*, a plant typical of south-eastern Asia, or of *Isatis tinctoria*, a plant typical of western and central Asia but also Europe. In the latter case, the colourant is known as *woad*. The structures of the main molecules present in indigo and woad are shown in Fig. 6. Indigo and woad were used as textile dyes at least since the second millennium BC in Egypt (Cardon 2007); being vat dyes and insoluble in water, as Tyrian purple, they were used as pigments in painting since at least the second millennium BC (Schweppe 1997). It is not easy to give accurate references with concern to indigo and woad because, from a diagnostic point of view, the distinction is very difficult if possible, and certainly not possible with non-invasive methods. Therefore, most of the information available must refer to ancient literary sources. We know that Pliny the Elder cites indigo (Nat. Hist. XXXV, 27) as a product coming from India.

Again, it must be noted that the addition of a white substrate does not mean the transformation of indigo into a lake but rather the need of changing its original greenish or blackish tone, not very pleasant, into a more pleasant tone by mixing with white. Cennino Cennini (Frezzato 2009) talked about the preparation of indigo mixed with a white pigment to simulate the brilliant aspect of azurite (chapter LXI): "…*togli indaco baccadeo, e trialo perfettissimamente con acqua; e mescola con esso un poco di biacca, in tavola; e in muro, un poco di bianco sangiovanni*" ("take indigo from Baghdad, and grind it perfectly with water; and mix it with a little white lead on the panel; and [if you want to paint] on the wall, [mix it with] a little St. John's white"). It is remarkable the annotation that indigo was called by Cennini *baccadeo*, that is from Baghdad, at those times the hub for the commerce of several goods from Asia. It is a further testimony that European painters used indigo for painting and not woad, and therefore that indigo was to be considered as a precious item. The price for Baghdad indigo was several times higher than woad, considering the need to justify the importation costs (Balfour-Paul 2016).

As Tyrian purple, indigo is a lightfast pigment, with a slow—though significant—tendency to fade. It is also considered suitable for fresco painting, due to its chemical resistance in alkaline medium. Cennini cites its use to imitate ultramarine blue in fresco painting (chapter LXXV): "*Se vuoi fare un vestire in fresco simigliante all'azzurro oltramarino, togli indaco con bianco sangiovanni*" ("If you want to make a hue similar to ultramarine blue in *fresco* painting, mix indigo with St. John's white").

The identification of indigo follows that of Tyrian purple in terms of relative ease. FORS analysis can identify it according to the typical absorption at ca. 650 nm (Aceto et al. 2014); elemental analysis, however, is of course useless. As for Tyrian purple, Raman spectroscopy (Karapanayiotis et al. 2004) can provide a fingerprint identification in conventional mode. HPLC can be used in order to discriminate between indigo and woad (Witkowski et al. 2017).

Indigo and woad were widely used in painting. The number of identification is high (some of them are reported in Table 4); it is possible that further identification is possible upon application of more powerful techniques, especially in situations where the pigment could be faded.

Further identification of indigo on wall paintings is to be found in artworks of Chinese culture, considering the long history of its use in Far eastern Asia (Zhu et al. 2016 and references therein).

Maya blue

A further indigoid pigment is *Maya blue*. This term has been given to the pigment found for the first time in 1931 on the wall paintings of the Temple of the Warriors at the Mayan site of Chichén Itzá, in Yucatán (Merwin 1931), but there is no archaeological evidence to attribute its invention to the Mayan culture rather than to other Mesoamerican cultures; in fact, it has been found in painted artworks of Aztec (Sánchez del Río et al. 2011), Zapotec (Alderson 2002), Teotihuacans (Doménech-Carbó et al. 2012) and other cultures.

Maya blue is a sort of synthetic organic/inorganic lake in which indigo, extracted from local plants such as *Indigofera suffruticosa*, is encapsulated inside the channels of a clay of zeolithic type, one of which is palygorskite or attapulgite. The pigment has notable properties in terms of chemical and physical resistance, which are imparted to indigo by the palygorskite cage. The interaction between indigotine molecules and palygorskite has been described in several scientific studies (Chiari et al. 2003; Doménech-Carbó et al. 2019; Caliandro et al. 2019) but not totally elucidated; it is remarkable, however, the fact that it can be truly considered as a nanotechnology dating back at least 2000 years (Chiari et al. 2008).

The production and the use of Maya blue have been attested at least since the Classic Period of the Mayan culture, i.e. between 300 and 1000 AD, up to the Spanish conquest in sixteenth century. Later studies, however (Vázquez de Ágredos Pascual et al. 2011) dated back the first use to the Pre-Classic period (around 150 AD) and recently (Vázquez de Ágredos-Pascual et al. 2019), it has been hypothesised a further backdating to at least 250 BC and the evidence that the technology of production could have been developed by another Pre-Hispanic culture of Western Mexico, the Chupicuaro.

The identification of Maya blue relies on the possibility of its distinction from indigo. This can be obtained with

Table 4 List of identification of indigo/woad in wall paintings

Date	Provenance	Location	Object/samples	Technique[1]	Reference
13th BC	Mycenean	Thebes, Greece	Painted plaster	Raman	Brysbaert (2008)
1st AD	Nabatean	Petra, Jordan	Wall paintings	PLM	Akrawi and Shekede (2010)
1st AD	Roman	Terme degli Stucchi Dipinti, Rome	Painted fragments	GC–MS	Gismondi et al. (2018)
6th AD	Asian	eastern Turkey	Wall paintings	PLM	Riederer (1977)
9th AD	Islamic	Samarra, Iraq	Painted stuccoes	Raman	Burgio et al. (2007)
9th–10th	Chinese	Mogao caves in Dunhuang, China	Wall paintings	HPLC–MS	AA.VV. (2013)
10th–14th	Italian	Santi Stefani crypt, Lecce (Italy)	Wall paintings	Raman	Fico et al. (2016)
11th AD	Tibetan-Buddhist	Xialu Temple, Tibet	Wall paintings	PLM	Yong and Shiwei (2014)
11th AD	Byzantine	Rock-Hewn Church, Şahinefendi (Turkey)	Wall paintings	Raman	Pelosi et al. (2016)
11th–12th	Tibetan-Buddhist	Nako Monastery, Northern India	Wall paintings	Raman	Bayerová (2018)
12th AD	Tibetan-Buddhist	Sumda Chun Monastery, Ladakh	Wall paintings	PLM	Gill et al. (2014)
12th AD	English	Synagogue, Guildford, UK	Wall paintings	Raman	Howard (2003)
13th AD	Tibetan-Buddhist	Sumtsek temple, Alchi, Ladakh	Wall paintings	PLM	Goepper et al. (1996)
13th–14th	English	Westminster Abbey, London	Wall paintings	PLM	Howe (2006)
13th–16th	English	several places in UK	Wall paintings	various	Howard (2003)
14th AD	Tibetan-Buddhist	Three-storied temple, Wanla, Ladakh	Wall paintings	PLM	Oeter and Skedzuhn-Safir (2015)
14th AD	Tibetan-Buddhist	Tsuglagkhang in Kanji, Ladakh	Wall paintings	PLM	Skedzun et al. (2013)
14th–15th	Indo-Tibetan	Saspol caves, Ladakh	Wall paintings	IRFC	Pinto et al. (2018)
16th AD	Italian	Santa Maria della Steccata, Parma (Italy)	Wall paintings	Raman	Bersani et al. (2004)
16th–17th	Spanish	Augustinian ex-convents in Mexico	Wall paintings	Raman	Ruvalcaba-Sil et al. (2017)
17th–18th	Spanish	Colonial missions, Chihuahua, Mexico	Wall paintings	FORS	Casanova-González et al. (2020)
18th AD	Andean	various	Wall paintings	Raman	Tomasini et al. (Tomasini et al. 2018)

[1] *FORS*, fibre optic reflectance spectrophotometry; *GC–MS*, gas chromatography–mass spectrometry; *HPLC–MS*, high-performance liquid chromatography–mass spectrometry; *IRFC*, infrared false colour; *PLM*, polarised light microscopy; *Raman*, Raman spectroscopy.

Raman spectroscopy (Leona et al. 2004; Giustetto et al. 2005; Sánchez del Río et al. 2006b; Manciu et al. 2007) according to the change in spectral features caused by the interaction between indigo and palygorskite.

Maya blue was particularly suitable for wall paintings due to its chemical-physical features, which allowed it to remain unaltered for hundreds of years even in harsh climates such as the tropical Mesoamerican lowlands. Its use is therefore attested in a great number of wall paintings from the Pre-Classical Mayan Period onwards. While until the 1990s it was thought that the use of Maya blue had ceased after the conquest of Mexico by the Spanish in 1521 and in any case limited to the continental area of Central America, subsequent analytical evidences were given of some continuity and diffusion in the use and/or production of the pigment. In fact, despite the replacement of native products with European technologies imposed by the new rulers, in many Augustinians, Dominicans and Franciscans convents built during sixteenth century in Mexico artists used Maya blue for decorating wall paintings (Sánchez del Río et al. 2006a), perhaps in an attempt of combining Christianity and Prehispanic culture. In addition, the pigment was found in wall paintings in Cuba between the eighteenth and the nineteenth century (Tagle et al. 1990), possibly as a consequence of the commercial link established between Mexico and Cuba in that period; indeed, accounts of Cuban merchants dealing in pigments attested that *New Spain* (i.e. Mexico) was among the sources of their imports. Considering the previous finding, the hypothesis made on a stylistic basis, but without diagnostic evidence, that in the seventeenth century Mexican artists of the Baroque era used Maya blue for their works (Van Houten Maldonado 2018) could have credit.

Identification methods

The identification of the organic colourants in wall paintings is generally more difficult than the identification of the inorganic ones. This is due to a combination of unfavourable factors:

- Organic compounds have intrinsically lower chemical stability that can only get worse in the case of wall paintings, so that in many cases we are facing relics of the colourants and not the original composition.
- Organic compounds have also lower physical stability: as specified in the introduction, most of them are fugitive, i.e. they tend to lose colour due to the action of light, so that they become unrecognisable.

- From a purely spectroscopic point of view, most of the dyes have high molar extinction coefficients: this means that they can generate hues at relatively low concentrations, so that the artists could use them with little amounts in paints; their identification, therefore, requires highly sensible techniques.
- The complexity of the composition: with no exception, all organic colourants are mixtures of two or more compounds, so that in many cases separative techniques are requested in order to have a reliable identification.
- In addition to the previous point, it must be considered that single molecules can be common to different dyestuffs, so that in order to identify a specific dye it is better to characterise the distribution of its major components, or at least to look for its specific markers.
- The production of lakes starting from clippings of dye cloths (Kirby et al. 2017), cited before with concern to red dyes and lakes, involves a possible fractionation of the original chemical distribution and, consequently, the onset of variable patterns which render more difficult the identification of the original material.
- The composition is rendered even more complex in cases where contamination occurs by materials used in restoration interventions, such as the application of egg-based fixatives or synthetic resins, that are mostly of organic nature.
- Finally, being organic colourants composed only by light elements (H, C, O, N, more rarely P and S), all elemental techniques, e.g. X-ray fluorescence spectrometry (XRF), scanning electron microscope–Energy dispersive X-ray spectroscopy (SEM–EDX) or proton induced X emission spectroscopy (PIXE), are of little use for their identification. There is a single, notable exception: the indirect identification of Tyrian purple is made possible by the presence of two bromine atoms in the structure of 6,6′-dibromoindigotine. This feature has been exploited in several instances, in particular in diagnostic works on Minoan paintings (Aloupi et al. 2000; Maravelaki-Kalaitzaki and Kallithrakas-Kontos 2003; Sotiropoulou 2004) but also in Roman paintings (Coccato et al. 2020).

General information on the identification and characterisation of dyes and lakes on artworks can be found in the reviews by Degano et al. (2009) and by Shahid et al. (2019).

Being dyes and lakes composed of poorly volatile compounds, the most powerful and commonly used technique for the identification of organic colourants is by far HPLC coupled with MS and/or DAD. Some reviews on this topic were given by Lech et al. (2009) and by Zasada-Kłodzińska et al. (2020). One major drawback of HPLC, and in general of the application of separative techniques to organic colourants, is that a preliminary step is always needed in order to take into solution the chemical markers from the sample. This can introduce some uncertainty in the subsequent results, as the recovery of molecules depends strictly on pH, time and temperature of extraction, etc. Acids such as formic hydrochloric, hydrofluoric, oxalic can be used, either with or without methanol. It is difficult to find a solution valid for all the colourants, however. The wide literature existing on the extraction of dyes from textile samples is poorly useful, being different the type of interaction between colourant and support. Wouters et al. (2011b) compared different methods of hydrolysis for the extraction of organic colourants from pigments and paints, finding that hydrofluoric acid followed by hydrochloric acid was the best solution; another suitable solution was oxalic acid followed by hydrochloric acid.

Another powerful technique, though less used than HPLC in this field, is GC–MS (Degani et al. 2014; Sutherland 2019). Usually, the gas-chromatographic analysis of organic colourants involves a derivatisation step in order to render more volatile the compounds present. Silanizing agents such as hexamethyldisilazane (HMDS) (Casas-Catalán and Doménech-Carbó 2005) and N,O-bis(trimethylsilyl) acetamide (BSTFA) (Degani et al. 2015) or etherification agents such as m-(trifluoromethyl) phenyltrimethylammonium hydroxide (TMTFTH) (Poulin 2018) can be used for the purpose.

As to spectroscopic techniques, the most suitable is undoubtedly surface enhanced Raman scattering (SERS) that provides the necessary sensitivity to identify dyes and lakes even at extremely low amounts. The works by Leona et al. (2006), Bruni et al. (2011) and Brosseau et al. (2011), among others, can be acknowledged as reference works for the identification of organic colourants on painted artworks. The application of conventional Raman spectroscopy, i.e. without aid by SERS substrates, is limited to the identification of organic pigments, that is indigo/woad and Tyrian purple (Karapanayiotis et al. 2004), verdigris (San Andrés et al. 2010) and copper resinate (Conti et al. 2014).

Other spectroscopic techniques to be cited in the identification of organic colourants are UV–visible diffuse reflectance spectrophotometry with optic fibres (FORS) (Aceto et al. 2014) and FT-IR spectrophotometry (Manfredi et al. 2017). Both techniques, though having lower diagnostic power than SERS and Raman spectroscopy, show the advantage that can provide a totally non-invasive identification (as to FT-IR spectrophotometry, this is valid when used in reflectance mode). Interesting and powerful extensions of reflectance spectrophotometry are multispectral and hyperspectral imaging in the visible and near-infrared ranges (Cucci et al. 2016; Cavaleri et al. 2017) that allows identification of some dyes and lakes, in particular madder, brazilwood, and cochineal (Vitorino et al. 2015) on large painted artworks, so they seem to be promising methods for analysis of wall paintings. The same holds true for multispectral photo-induced luminescence imaging, a group of techniques useful for detection and mapping of madder on painted artworks (Dyer and Sotiropoulou 2017). A general description of multispectral imaging methods is contained in Dyer et al. (2013).

Finally, the role of microspectrofluorimetry must be also cited (Melo and Claro 2010; Idone et al. 2017), though it is usually a micro-invasive technique.

There is a slight difference between the *identification* and the *characterisation* of an organic colourant. In the first case, we can have preliminary, easy-to-obtain results from spectroscopic techniques such as FORS or FT-IR spectrophotometry and a fingerprint identification with Raman or SERS spectroscopy. In the second case, the characterisation of the distribution of compounds presents in an organic colourant allows in many cases the identification not only of the colourant itself, but also of the vegetal or animal source. This requests of course more powerful techniques such as the chromatographic ones.

Although there may be differences in the application of organic colourants between paintings on inorganic supports (i.e. wall paintings, polychrome pottery and painted stone artworks) and paintings on organic supports (i.e. canvas paintings, miniature painting), from the diagnostic point of view the differences are very few. Since organic colourants are never used in *buon fresco*, the binding media used in wall paintings will be similar to those used on canvas, i.e. egg tempera, gums, waves, siccative oils and many others as described by Casadio et al. (2004). The interactions between dyes and lakes and their binding media are therefore similar as well.

One drawback can arise when one wants to distinguish between a dye and its lake. Using spectroscopic and chromatographic techniques would hardly reveal differences; elemental analysis could be useful in order to identify key elements typical of the inorganic supports, such as Al (from alum and aluminium hydroxide), Pb (from lead white), Si (from clays or earths) or Ca (from chalk, limestone or shell), but these are all common elements in wall paintings, deriving from paints and/or intonaco layers; therefore, their specific presence as lake supports must be verified with techniques with high spatial resolution such as SEM–EDX, to be used on micro samples.

Concluding summary of key concepts

The use of organic colourants in wall paintings, polychrome pottery and painted stone artworks has been given little attention in the past, perhaps on the assumption that they were rarely used by ancient artists. A survey on the scientific literature, however, reports a large number of diagnostic evidences and despite the lack of specific publications on the subject, it appears that there has been continuity through the centuries in the use of such colourants in painted artworks on inorganic supports, at least with regard to the most important such as madder, Tyrian purple and indigo. In several studies among the older ones, the results reported the occurrence of a generical "organic lake" or "organic colourant". This typically occurred for red lakes. The application of powerful micro-invasive techniques such as SERS, HPLC–MS and other chromatographic techniques has been greatly increased in the last 20 years, allowing to obtain more precise, sensitive and informative identification. As an example, it is common practice now going beyond the identification of "a red lake" and providing full characterisation of the different red anthraquinone lakes. In a recent work, Gismondi et al. (2018) applied GC–MS to micro samples of paints taken from first century Roman wall paintings. Authors were able to identify a high number of metabolites of vegetal species, among which some that could possibly derive from at present unknown colourants. Such study was an example of the wide information that can be disclosed by the systematic application of chromatographic techniques to the analysis of micro samples from wall paintings.

It is advisable that future studies on wall paintings, polychrome pottery and stone will systematically involve the application of micro-invasive separative techniques, in order to have a better understanding of the use of organic colourants. In this way, new information will be gathered with concern to artistic techniques, biological sources and trade routes, which will allow to have a clearer view of the use of these wonderful and mysterious colourants.

Funding Open access funding provided by Università degli Studi del Piemonte Orientale Amedeo Avogrado within the CRUI-CARE Agreement.

Data availability Data sharing is not applicable to this article as no new data were created or analysed in this study.

Declarations

Conflicts of interest The authors declare that they have no conflicts of interest.

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