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Characterisation and discrimination of various types of lac resin using gas chromatography mass spectrometry techniques with quaternary ammonium reagents

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ABSTRACT

A variety of lac resin samples obtained from artists' suppliers, industrial manufacturers, and museum collections were analysed using gas chromatography mass spectrometry (GCMS) and reactive pyrolysis GCMS with quaternary ammonium reagents. These techniques allowed a detailed chemical characterisation of microgram-sized samples, based on the detection and identification of derivatives of the hydroxy aliphatic and cyclic (sesquiterpene) acids that compose the resin. Differences in composition could be related to the nature of the resin, e.g. wax-containing (unrefined), bleached, or aged samples. Furthermore, differences in the relative abundances of aliphatic hydroxyacids appear to be associated with the biological source of the resin. The diagnostic value of newly characterised lac components, including 8-hydroxyacids, is discussed here for the first time. Identification of derivatised components was aided by AMDIS deconvolution software, and discrimination of samples was enhanced by statistical evaluation of data using principal component analysis. The robustness of the analyses, together with the minimal sample size required, make these very powerful approaches for the characterisation of lac resin in museum objects. The value of such analyses for enhancing the understanding of museum collections is illustrated by two case studies of objects in the collection of the Philadelphia Museum of Art: a restorer's varnish on a painting by Luca Signorelli, and a pictorial inlay in an early nineteenth-century High Chest by George Dyer.

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1. Background

1.1. Origin, varieties and uses of lac resin

Lac resin is the secretion of scale insects (*Kerria lacca*, *Kerria chinensis*, and related species) cultivated mainly in India, Thailand and other parts of Southeast Asia [1–3]. The material forms a dense encrustation on the branches of host plants infested by the insects, and when harvested in this form it is referred to as stick-lac. After crushing and washing in water to remove plant matter, insect remains, and a red colourant (lac dye), the semi-refined material is known as seedlac. Further processing involves heating and filtering the seedlac through a cloth or wire mesh, or solvent extraction, to produce the various grades of commercial resin. This is supplied in the form of small medallions (button lac) or, more commonly, stretched or spread into thin sheets and broken into small fragments; in this latter form the resin is known as shellac. Various grades of shellac are produced, categorised mainly according to their colour – e.g. garnet, orange, lemon and blonde – or with reference to the strain of insect or season of harvest (*kusmi*, *bysakhi*, etc.) Additional processing can include chemical (hypochlorite) bleaching, to produce a highly transparent grade of resin known as bleached or "white" shellac, and/or refining to remove a naturally occurring wax component. More detailed discussions of lac resin and its processing can be found in the literature [4–6].

Although the major commercial markets for shellac are for architectural applications (wood finishes) and coatings for pharmaceuticals and food [7], this paper is concerned with its study in works of art and cultural artefacts. Lac resin is of great historical interest because of its use for centuries for a variety of purposes such as an adhesive, coating (varnish) or decorative inlay material. A precise characterisation of the resin in museum objects can provide information on artistic and restoration practices, shed light on alteration and deterioration processes, and inform safe and effective treatments essential for their preservation.

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1.2. Composition and analysis

The chemistry of lac resin is complex and not fully understood, although several published reviews provide a useful overview [6,8]. The dye and wax components of the raw material combined make up c. 10–15% of the total. The major, resinous component is a mixture of mono- and polyesters formed from hydroxy aliphatic acids, primarily 9,10,16-trihydroxy palmitic or aleuritic acid, linked with cyclic sesquiterpene acids of various structures. A major sesquiterpene in the fresh resin is jalaric acid, a monocarboxylic acid with one aldehyde and two hydroxy groups, along with a smaller proportion of laccijalaric acid, a related compound with a single hydroxy group. The resin fraction has been described in terms of 'hard' (ether-insoluble) and 'soft' (ether-soluble) resin components, along with additional sub-divisions, although these categories are somewhat arbitrary and differentiated mainly on the basis of the molecular weight of the ester oligomers. Fig. 1 shows the approximate (average) structure for 'pure lac resin', a fraction isolated from the hard resin, comprising four molecules each of the aleuritic and terpene acids [6,9], along with structures of the principal hydroxyacids.

A number of analytical techniques have been applied to the study of lac resin, with spectroscopic methods most widely used in the cultural heritage field. Fourier transform infrared spectroscopy (FTIR) is well-established [10], and complementary techniques such as far-IR, Raman and fluorescence spectroscopy have been explored more recently [11–14]. Although spectroscopy can be useful to indicate the presence of lac resin, it is not generally reliable for the specific identification of natural resins when aged and/or present in mixtures, as is often the case with samples obtained from museum objects [15]. Because of the unique chemistry of lac resin – as compared to other resinous materials derived from plants (di- and triterpenes) or modern synthetic polymers – the most effective and definitive methods for its identification in complex, microscopic-sized samples are based on mass spectrometry and chromatography. Some promise has been shown by the use of matrix- and graphite-assisted laser desorption ionisation mass spectrometry (MALDI, GALDI) [16,17], but the most detailed compositional information has been provided by GCMS and Py-GCMS, which allow the separation and identification of the characteristic hydroxy aliphatic and terpene acids (and in wax-containing grades, the wax components also). Several protocols for the analysis of lac resin have been published, including the use of Py-GCMS without derivatisation [18]: the value of this approach is limited because of the numerous hydroxy and carboxylic acid groups in the lac constituents, however, and more reliable characterisations have been achieved by the use of silylating [19] or methylating reagents [20–22] to produce derivatives with improved chromatographic properties. In this study both GCMS and Py-GCMS were used with quaternary ammonium methylating reagents: (*m*-trifluoromethylphenyl)trimethylammonium hydroxide (also known as trimethyl[α,α,α-trifluoro-*m*-tolyl]ammonium hydroxide or TMTFTH, and available commercially as 'MethPrep II' [23]) for GCMS, and tetramethylammonium hydroxide (TMAH) for Py-GCMS.

TMTFTH and TMAH have gained widespread use for the study of organic materials in works of art since they give efficient derivatisation without complicated sample pretreatment or extraction steps – an important consideration for samples that are often very small and complex [23–32]. Whereas TMAH is typically used with a pyrolysis interface, TMTFTH has been shown to be effective at lower temperatures and can therefore be used readily without a pyrolyser, by injection of a sample/reagent solution directly into a conventional GC inlet. TMTFTH is also favoured by some researchers since it has a lower alkalinity and avoids some undesirable side-reactions, such as isomerisation of polyunsaturated fatty acids, that can occur with TMAH [23,24,29,31,32]. The use of TMAH with Py-GCMS is commonly termed 'reactive' Py-GCMS or thermally assisted hydrolysis and methylation Py-GCMS (THM-Py-GCMS). Both reagents act by promoting the hydrolysis of the resin (poly)esters and methylation of free acid and (to some extent) alcohol groups to produce volatile methyl esters and ethers [23,24,33]. A complication of TMTFTH is that it can produce (trifluoromethyl)phenyl (TFMP) ethers, in addition to methyl ethers, upon reaction with certain alcohols [34,35]: although these compounds are essentially artefacts and complicate the interpretation of data, as discussed below, they have the serendipitous advantage of producing mass spectra that are distinctive and diagnostic, and thus have value as chemical markers.

This paper presents comparative data from the analysis of a wide variety of reference samples of lac resin from commercial artists' suppliers, industrial manufacturers, and museum collections using the two analytical approaches. Aspects of this research dealing specifically with bleached shellac and its use as a varnish for paintings have been described in separate papers [21,22]. Whereas some previous research has treated shellac as a generic material, without attempting to discriminate different varieties, this study represents a significant advance in the characterisation of the resin, highlighting the potential to differentiate lac resins of different grades, ages and biological/geographical sources. Discrimination is enhanced by statistical evaluation of the (Py)GCMS data using principal component analysis. Mass spectra for selected diagnostic derivatives, most of which are previously unpublished, are provided in an Appendix. The value of the analytical approaches is illustrated by two case studies of objects in the collection of the Philadelphia Museum of Art (PMA): a restoration varnish on a painting by Luca Signorelli (c.1445-1523) and a pictorial inlay in an early nineteenth-century High Chest by George Dyer (active 1805-46).

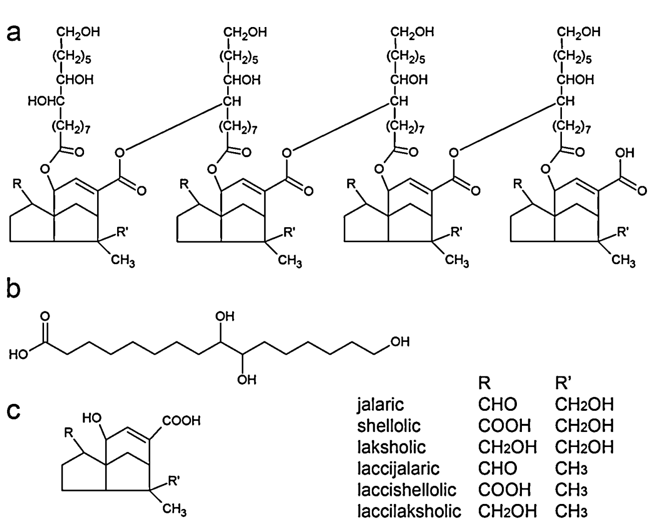

Fig. 1. Generalised structure of "pure lac resin" (a), with structures for aleuritic acid (b) and cyclic terpene acids (c) that are the major compounds obtained by hydrolysis of the resin esters.

2. Experimental

2.1. Samples

45 samples of lac resin, representing a range of characteristics such as grade, age, and geographical origin, were obtained for analysis as listed in Table 1. Aleuritic acid was supplied by Sigma–Aldrich, St. Louis, MO 63178, USA. Samples of varnish from the Signorelli painting and inlay material from the Dyer High Chest

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