

Raman spectroscopy of coloured resins used in antiquity: dragon's blood and related substances

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Abstract

Dragon's blood is a deep red resin which has been used for centuries by many cultures and much prized for its rarity, depth of colour and alchemical associations. The original source of dragon's blood resin is believed to be *Dracaena cinnabari* from Socotra in Africa, but since mediaeval times there have been several alternatives from different geographical locations from the Canary Islands to the East Indies. Here, the Raman spectra of dragon's blood resins from *Dracaena draco* Liliaceae trees growing in several different locations bordering the Mediterranean and Middle East are compared with the resins from alternative botanical sources such as *Daemonorops draco*, *Dracaena cinnabari* and *Eucalyptus terminalis*, which all generically come under the description of dragon's blood. Key vibrational spectroscopic marker bands are identified in the Raman spectra of the resins, which are suggested for adoption as a protocol for the identification of the botanical and possible geographical sources of modern dragon's blood resins. The Raman spectra of materials, which are falsely attributed to dragon's blood resin are also shown for comparison and identification purposes. Changes in the Raman spectra of genuine dragon's blood resin specimens arising from simple processing treatment during the preparation of the resins for sale are also identified, which suggests a possible attribution characteristic for unknown samples. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Spectroscopy; Dragon's blood; Liliaceae trees

1. Introduction

The natural resin 'dragon's blood' has been used in antiquity for diverse medical and artistic purposes; it was renowned for its deep red colour and it formed a staple of mediaeval alchemy (Fig. 1). Many ancient legends describe the growth of a dragon tree on the spot where mythical beasts fought to death with a dragon [1]. Unlike other plant resins, dragon's blood is exuded from the fruit of the tree rather than from the tree-trunk or

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the leaves. Originally, the *Dracaena draco* (Liliaceae) trees on Socotra were believed to be the source of much of the ancient supply of dragon's blood resin but alternative sources from mediaeval times in the Canary Islands (Tenerife), Madeira and the East Indies have also been identified [2,3].

Dragon's blood resin is harvested as deep red teardrop-shaped lumps, separated physically from the fruit, which on pulverization produce a deep crimson powder; whereas most natural resins owe their colour to minor acidic components and the depth of colour is sensitive to the pH, dragon's blood resin colour is pH-independent and the major constituents are themselves highly coloured [4]. The medicinal applications of dragon's blood resins have been ascribed to the presence of benzoic acid, whose stringent antiseptic properties still make the resins a natural remedy in some cultures today [5].

Several cultures have at least one indigenous resin which can be termed dragon's blood but the botanical sources are often dissimilar; at least two distinct types of true dragon's blood resin have been recognised, from *Dracaena* and *Dae-monorops spp.* species. Resins from the fruit of the South–East Asian rattan- or cane-palm, *Dae-monorops draco* (Palmae), is the principal source for commercially harvested dragon's blood today; primary sources of the resin in Western antiquity since the Roman Empire were almost certainly

from *Dracaena draco* Liliaceae from the Canary Islands and *Dracaena cinnabari* Liliaceae, which was once prevalent around the Mediterranean coast but now endemically localized to the island of Socotra, off the Horn of Africa. Other modern and ancient sources of dragon's blood resin substitutes are *Croton draco* (Mexico) and *Eucalyptus resinifera* (Australia) [6]; *Croton lechleria*, from Euphorbiaceae family in the Amazon forest, is also named dragon's blood, and today is used for antibacterial, anti-hemorrhagic and other properties [7]. A powdered dark red coral from the Indian Ocean is still sold in Yemeni bazaars as 'dragon's blood'. A very recent publication [8] reports the use of dragon's blood from *Dae-monorops draco* as an incense and was mixed with marijuana and smoked as an alternative to opium.

In an earlier study, FT-Raman spectroscopy was applied [9] to the characterization of dragon's blood resins and particularly to those which had been collected from *Dracaena cinnabari* (Liliaceae) in East Africa in the 1990s. Here we report the Raman analysis of *Dracaena draco* resins from several geographical locations from which a possible protocol for source discrimination is suggested in comparison with the *Dracaena cinnabari* and other 'dragon's blood' resins.

2. Experimental

2.1. Samples

Dragon's blood resins of the species *Dracaena draco* (L.) were obtained from several geographical locations, currently archived in the Royal Botanic Gardens Collection, Kew, comprising:

1. Catalogue number 36825; 175.06; gum resin exuded from the Great Dragon Tree, Tenerife, Canary Islands, collected by Dr Lehmann;
2. Catalogue number 36516; resin sticks wrapped in leaves, Socotra, from Pharmacy Society collection, UK, ref. 36.A1;
3. Catalogue number 36653; resin from Funchal, Madeira, presented to the Pharmacy Society collection, UK, by Gerarde Jose de Nobrego;
4. Catalogue number 36824; resin from Lisbon Botanic Gardens, Portugal, collected by M. Welwitsch.



Fig. 1. "According to alchemists a dragon inspired could be transformed into a philosopher's stone"; mediaeval woodcut engraving of alchemical mysticism surrounding dragon's blood and the search for the philosopher's stone. Many of the attributes required of alchemists then are necessary for research scientists today!

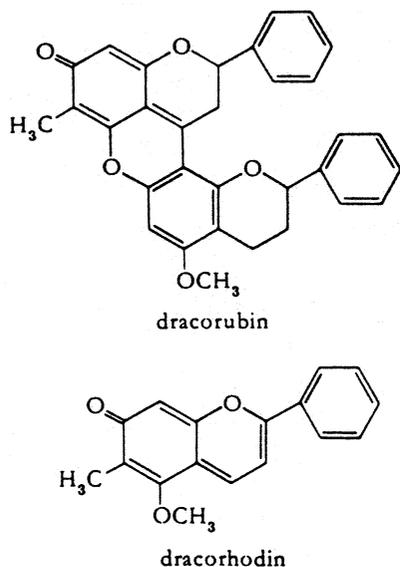


Fig. 2. Chemical formulae of dracorubin and dracorhodin, two colored falconoid constituents of dragon's blood resins.

Although the main purpose of the present study was the Raman spectroscopic characterization of these *Dracaena draco* resins, for comparison purposes specimens of other alternative dragon's blood resins were analyzed. These included *Dracaena cinnabari*, *Daemonorops draco* and *Eucalyptus terminalis* resins.

The chemical composition of natural resins and gums is dependent on their botanical and geographical sources [10–13] and a literature search reveals that more information is available about *Dracaena cinnabari* resins than their *Dracaena draco* and *Daemonorops draco* counterparts. *Dracaena cinnabari* resins contain biflavonoids and dihydrochalcones such as cinnabarone, dracoresene and dracoresinotannol [14–16] whereas *Daemonorops draco* resins contain dracoresinotannol, dracorubin, dracorhodin and abietic acid [17–19]. Dragon's blood resins are acidic, with acid values of 50–80 mg KOH per g, and a specific gravity of 1.21 g.ml⁻¹. They melt over a temperature range of between 85–95 °C. From their use in ancient medicine, it is believed that dragon's blood resins also contain benzoic acid [17]. Some molecular structures of the most important examples of the constituents of dragon's blood resins are shown in

Fig. 2; a product of bond scission in dracorubin is dracoic acid, which contains both phenolic hydroxyl and carboxylic acid groups, seen in the dracorhodin structure, which probably accounts for the suspected presence of benzoic acid in some resins [18].

2.2. Fourier-transform raman spectroscopy

Good quality Raman spectra were obtained using a Bruker IFS 66 spectrometer with an FRA 106 Raman module attachment and Nd³⁺/YAG laser excitation at 1064 nm. To prevent sample degradation laser powers of about 10–20 mW were used and up to 4000 spectral scans accumulated with a 4 cm⁻¹ resolution; because of the intense blood-red colour of the resin specimens, the onset of thermal heating was possible and special care with sample presentation was necessary to minimise thermal degradation. A series of spectra was examined to ensure that longer accumulation times did not result in spectral degradation. Excitation with 20 mW power of frequency-doubled Nd³⁺/YAG radiation at 532 nm produced immediate sample decomposition and sample conflagration. Attempts to excite the Raman spectra of dragon's blood resins using 632.8 and 785 nm excitation were also unsuccessful and large fluorescent background emission was noted.

2.3. Results and discussion

The FT-Raman spectra of the *Dracaena draco* L. Resins and of related dragon's blood specimens are shown in Figs. 3–8; in these spectra the wavenumber regions 2600–3400 and 200–1800 cm⁻¹ have been selected, representing the CH stretching and skeletal stretching and deformation mode regions of the vibrational spectrum, respectively. The wavenumbers of the *Dracaena draco* L. Raman bands are tabulated in Table and proposed vibrational assignments have been made in accordance with previous studies of natural waxes, resins and biopolymers [12,13] [20–24]. In Table 2 a comparison is made between related dragon's blood specimens from several sources and a *Dracaena draco* L. wavenumber listing from Table 1 is included here too.

A comparison of the Raman spectra of *Dracaena draco* L. Resins from different geographical sources and with dragon's blood specimens from other botanical sources reveals some interesting conclusions with regard to the creation of a spectroscopic protocol for the differentiation of the resins from diverse sources:

1. The CH stretching region for the *Dracaena draco* L. specimens (Table 1) is similar for the Funchal and Lisbon specimens both in band wavenumbers and in relative band intensities; minor differences are a stronger band intensity for the 2912 cm^{-1} feature in the Lisbon specimen and the observation of a weak feature at 2882 cm^{-1} in the Funchal specimen. However, the Tenerife specimen of *Dracaena draco* L. resin has a significantly different appearance in this spectral region, in that the CH modes are much weaker in intensity than the other bands in the spectrum and the fine detail has been lost. This cannot be attributed solely to specimen degradation since the bands in the lower

wavenumber region are quite well-resolved and do not exhibit the characteristic diffuseness of degraded biomaterial that has been noted in previous studies of the Raman spectra of resins from archaeological excavations [10,20,25].

2. The CH stretching region in the *Dracaena draco* L. specimens studied has some similarity with the spectra of the *Dracaena cinnabari* resins studied earlier [9] in that the band at 3012 cm^{-1} assigned to aromatic ring stretching also occurs in both sets of botanical specimens; however, the bands at 2912 and 2882 cm^{-1} are absent from the *Dracaena cinnabari* specimens and the doublet at $2844, 2860\text{ cm}^{-1}$ in the *Dracaena draco* L. specimen of Funchal origin compares with a single band at 2850 cm^{-1} in the *Dracaena cinnabari* specimens from different locations.
3. The $200\text{--}1800\text{ cm}^{-1}$ wavenumber region for the *Dracaena draco* L., *Daemonorops draco*, *Dracaena cinnabari* and *Eucalyptus terminalis*

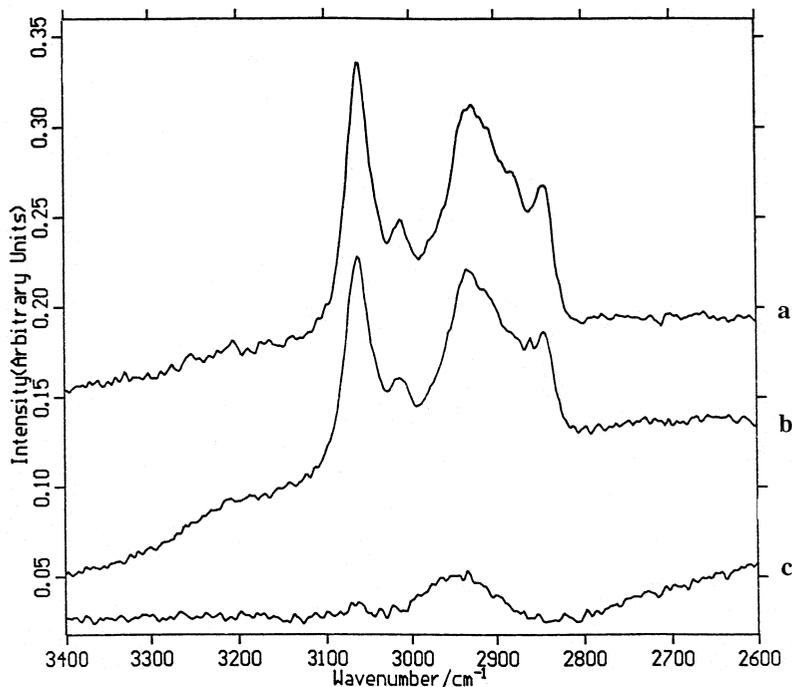


Fig. 3. Stack-plotted FT-Raman spectra of three *Dracaena draco* Liliaceae dragon's blood resin specimens: *a* Lisbon; *b* Funchal, Madeira and *c* Tenerife botanical locations. Excitation wavelength 1064 nm ; spectral resolution 4 cm^{-1} ; 4000 scans accumulated; wavenumber range, $2600\text{--}3400\text{ cm}^{-1}$.

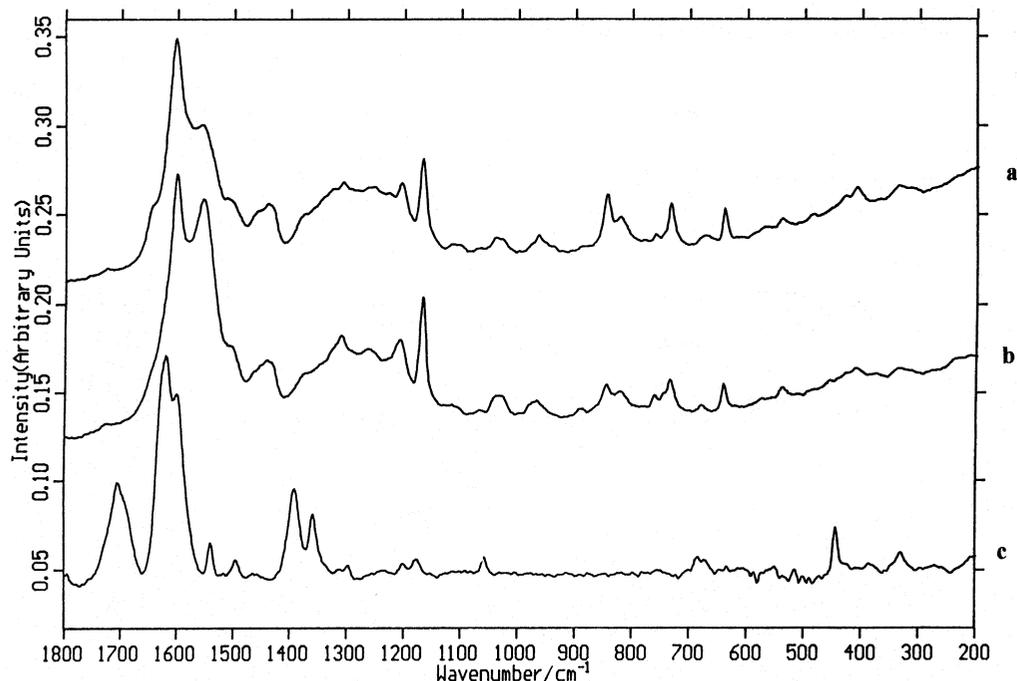


Fig. 4. As for Fig. 3 but wavenumber range, 200–1800 cm^{-1} .

botanical specimens of dragon's blood resin (Fig. 5) show subtle differences in their Raman spectra which reflect their diverse compositions. Although the Funchal and Lisbon specimens of *Dracaena draco* L. resins are superficially very similar in this wavenumber region, especially for the bands below 1500 cm^{-1} , the 1500–1750 cm^{-1} region reveals significant band intensity differences which are perhaps suggestive of a possible sourcing marker. For example, the two strongest bands in the spectra occur at 1604 and 1556 cm^{-1} and these are of almost equal intensity in the Funchal specimen spectrum but the 1557 cm^{-1} band is significantly depleted in intensity in the spectrum of the Lisbon specimen. Also, a weaker shoulder at 1660 cm^{-1} is clearly evident in the spectrum of the Lisbon resin but is absent from the spectrum of the Funchal resin. The vibrational modes that occur in this region are associated with C=C conjugated with C=O stretching; even in the parent simple molecule 1,4-benzoquinone there is much controversy in the literature over molecular assignments in this region [26,27].

4. An even larger difference between the Raman spectra of *Dracaena draco* L. specimens of Funchal and Lisbon origins and those of Tenerife origin is observed in Fig. 3, where the strongest band at 1604 cm^{-1} in the former resins is present only as a weak shoulder on the 1621 cm^{-1} band in the Tenerife sample. The Tenerife sample has no band at 1556–1557 cm^{-1} but a weaker band is seen at 1541 cm^{-1} , which has no counterpart in the spectra of the resins from Funchal and Lisbon.
5. The prominent doublet at 1393–1360 cm^{-1} in the Tenerife specimen has no counterpart in the spectra of the resins from Funchal and Lisbon but several other features of weaker intensity are possibly correlated. Similarly, the spectral region between 600 and 1000 cm^{-1} which shows several bands characteristic of both *Dracaena draco* L. resins from Funchal and Lisbon and *Dracaena cinnabari* resins are not observed in the resin specimen from Tenerife.

6. The two strong bands at 1550 and 1170 cm^{-1} could be related to chemical electronic conjugation that occurs in natural carotenoids, like bixin (1525 and 1155 cm^{-1} , respectively, to C=C and C–C bonds) [28], but in the case of the dragon's blood resin we have a more complex system involving C=C, C–C and C=O in conjugation.

The assignments in Tables 1 and 2 are necessarily subjective, given the complex compositions of the botanical resin specimens studied in the present work, but the observed differences must be related to primarily the flavanoids and diterpenes which comprise the major components of these systems. In similar studies of the Raman spectra of amber and copal resins from different geographical locations, recent work has centered on the diterpene and triterpene compositions of the resins related to their sources [29–33]. However, this work has been complicated by the age and maturity range of the specimens studied, often spanning some 30 million years, during which

the depletion of some components has occurred geologically or through exposure to different burial environments; the influence of atmospheric oxidation processes on the survival of chemical unsaturation in these materials is believed to be critical. This is certainly not the case in our present work since all the resin samples have been collected freshly and immediately lodged in botanical archives.

Dragon's blood resin is generically a complex mixture of flavanoids, exemplified by dracorubin and dracoic acid, their derivative chalcones and deep red aurones [34,35] from which the formation of benzoic acid produced as a result of acid or alkaline hydrolysis is realised. It has long been believed that the antiseptic properties of benzoic acid have contributed to the therapeutic uses of dragon's blood in antiquity; however, the characteristic Raman bands of benzoic acid, which include the strongest features at 794 and 1001 cm^{-1} do not appear in any of the resin spectra reported here. Hence, we can conclude that the amount of

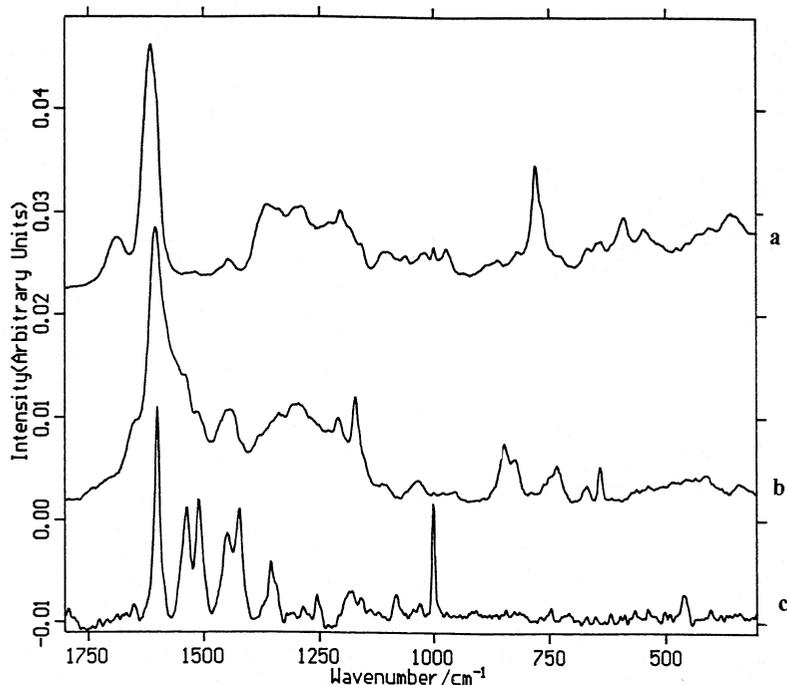


Fig. 5. Stack-plotted Raman spectra of three dragon's blood resins from different botanical specimens: *a* *Eucalyptus terminalis* (Australia); *b* *Dracaena cinnabari* (Socotra, East Africa); *c* *Daemonorops draco* (East Indies). Conditions as for Fig. 3 but wavenumber range 200–1800 cm^{-1} .

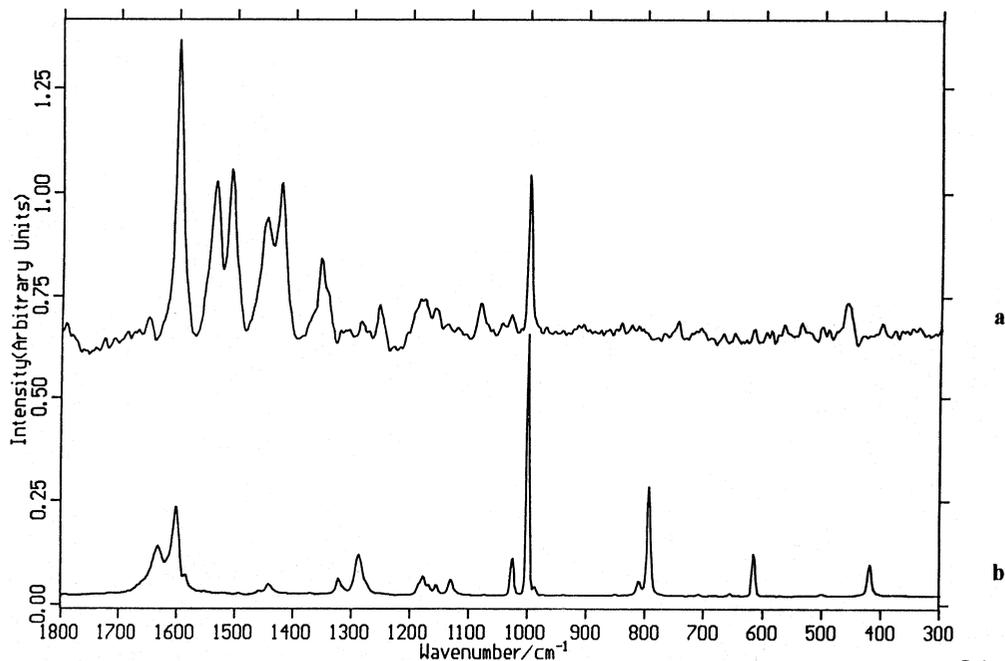


Fig. 6. FT-Raman spectra of *a* *Daemonorops draco* resin; *b* benzoic acid; conditions as for Fig. 3, but wavenumber range, 300–1800 cm⁻¹.

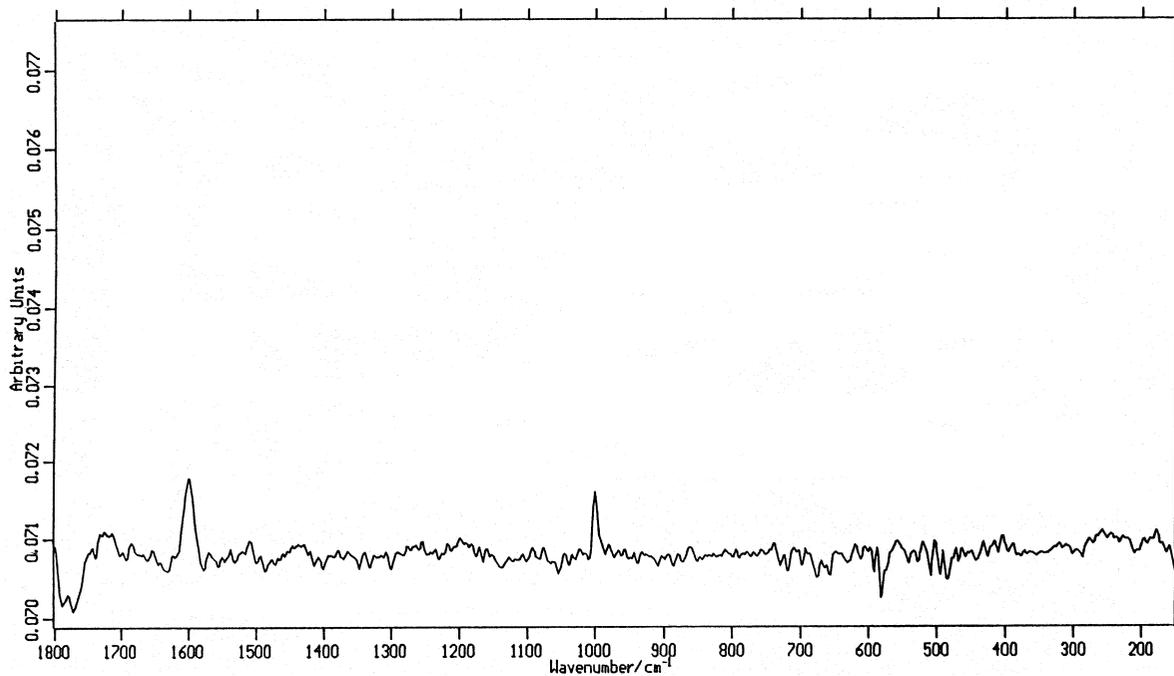


Fig. 7. FT-Raman spectrum of a Socotran resin believed to be from a *Dracaena draco* Liliaceae tree; conditions as for Fig. 3, but the simplicity of the spectrum relative to the spectra in Fig. 3 should be noted.

benzoic acid is either not detectable in the naturally harvested resins or that the benzoic acid arises from a post-harvesting treatment process which could cause the chemical scission of the flavanoids shown in Fig. 2. Such a process could be initiated by the melting and casting of resin into cakes or sticks, which are often reported to be wrapped in rattan- or cane-leaves prior to export and sale in the country of origin [17]. A sample of dragon's blood which was treated in this way has been examined and the Raman spectrum recorded is shown in Fig. 6 (origin: ex-A.F.Suter, Swan Wharf, London, sample no. 5059, source and provenance East Indies). The presence of the aromatic ring breathing wavenumber at 1001 cm^{-1} is not in itself sufficient to identify unambiguously the presence of benzoic acid residues in the resin sample, especially since the second marker band at 794 cm^{-1} is absent. It is possible that the pendant phenyl group in the dracorhodin or dracorubin (Fig. 2) could be responsible for this band in the Raman spectrum. Clearly, the chemical composition of the dragon's blood resin available commercially from the East

Indies source contains monosubstituted aromatic benzenoid compounds, not necessarily benzoic acid. It is also interesting to note that the spectrum of the processed resin shown in Fig. 6 has a small band at 460 cm^{-1} which is a signature for alpha-quartz; this is a constituent of fine river sand which has been recorded as an additive to aid the pulverisation of pigments-it is believed that its presence here reflects the post-harvesting treatment of the dragon's blood resin lumps prior to their preparation for sale. In this connection the appearance of the CH stretching region (not shown here) as a broadened, diffuse, unresolved feature in the Raman spectrum of the commercial sample confirms the pre-processing of the specimen as some evidence of chemical degradation has occurred.

Comparison of the Raman spectra of genuine dragon's blood resins with the more ubiquitous specimens of deeply coloured ambers reveals that there are but few points of similarity [29–33]. This is perhaps not surprising since the chemical characteristics of dragon's blood and amber resins are

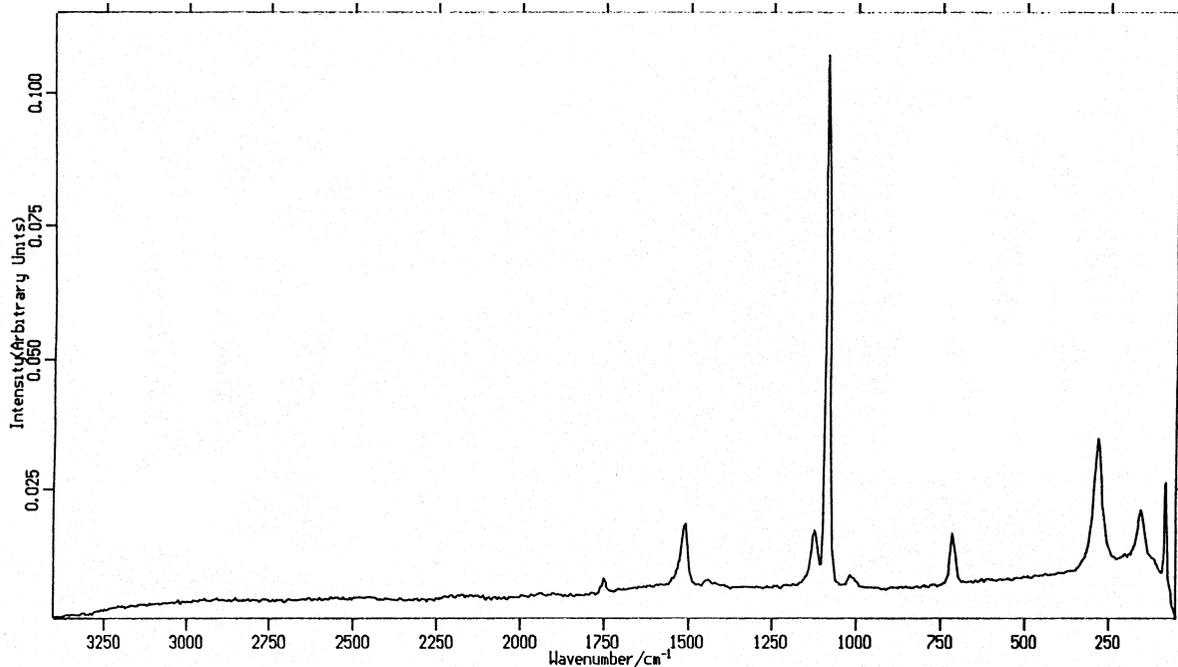


Fig. 8. FT-Raman spectrum of a blood-red powder from Al-Kuri, Aden, which is a substitute resin for dragon's blood resin. The spectral bands are clearly assignable to calcite (1087 , 715 , 284 and 156 cm^{-1}), aragonite (1019 cm^{-1}) and carotene (1508 and 1123 cm^{-1}); a trace of unidentified (organic or inorganic) matter is provided by the weaker features at 1740 and 1440 cm^{-1} .

Table 1

Vibrational wavenumbers (in cm^{-1}) and band assignments in the Raman spectra of *Dracaena draco* L. specimens of Dragon's blood from different sources

Tenerife specimen	Funchal specimen	Lisbon specimen	Approximate assignment of vibrational mode
3060 w	3062 m	3062 m	$\nu(\text{CH})$ olefinic
	3014 w	3012 w	$\nu(\text{CH})$ aromatic
2950 mw, br	2933 m	2927 m	$\nu(\text{CH}_3)$ sym
	2912 mw, sh	2912 w, sh	$\nu(\text{CH}_3)$ sym
		2882 w, sh	
	2860 w		$\nu(\text{CH}_2)$ sym
	2844 mw	2844 mw	$\nu(\text{CH}_2)$ sym
1704 m	1720 vw	1720 vw	$\nu(\text{C}=\text{O})$
1621ms		1660 mw, sh	$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{O})$
1602 ms, sh	1604 s	1604 s	$\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{O})$
	1556 s	1557 s	$\nu(\text{C}=\text{C})$ substituted aromatic ring
1541 w			$\nu(\text{C}=\text{C})$ substituted aromatic ring
	1509 w, sh	1510 w	$\nu(\text{C}=\text{C})$
	1443 m, br	1442 m, br	$\nu(\text{C}-\text{C}) + \delta(\text{CH}_2)$
1393 m			$\nu(\text{C}-\text{C}) + \delta(\text{CH}_2)$
	1382 w	1380 w	$\nu(\text{C}-\text{C}) + \delta(\text{CH}_2)$
1360m			$\nu(\text{C}-\text{C}) + \delta(\text{CCH})$
	1312 mw	1310 w	$\delta(\text{CH}_2)$
1300 m			$\delta(\text{CH}_2)$
	1266 w	1255 w	$\nu(\text{C}-\text{O}) + \nu(\text{C}-\text{C})$
1205 m	1209 mw	1208 mw	$\nu(\text{C}-\text{O}) + \delta(\text{CCH}) + \delta(\text{ring})$
1179 w	1170 ms	1170 ms	$\nu(\text{C}-\text{C}) + \delta(\text{CCH})$
	1113 w	1117 w	$\nu(\text{C}=\text{C})$
1060 w	1070 vw	1070 vw	$\nu(\text{C}=\text{O})$
	1040 mw	1041 mw	$\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{O})$
	969 mw	968 m	$\rho(\text{CH}_3)$
	889 w		$\rho(\text{CH}_2)$
	847 mw	848 ms	$\delta(\text{CCH})$
	830 w	824 m	$\omega(\text{CH})$
	763 w	765 w	$\omega(\text{C}-\text{O}) + \omega(\text{C}=\text{O})$
	735 mw	736 m	$\delta(\text{CCC})$ aromatic
680 w, br	680 w	674 w	$\delta(\text{CCC})$ aromatic
	642 mw	642 m	$\delta(\text{CCC})$ aromatic
		580 w	$\delta(\text{COC})$
	540 w	541 w	$\delta(\text{COC})$
445 mw			$\delta(\text{CCC})$
		430 w, sh	$\delta(\text{CCC}) + \delta(\text{CCO})$
	412 w, bv	412 mw	$\delta(\text{CCO})$

very different; however, this observation suggests a definitive role for Raman spectroscopy in the nondestructive discrimination between the two types of resin which have been used over many centuries for decoration and adornment. Ambers, and the geologically younger copal and kauri resins, are based on molecular diterpenoid and labdane structures with exocyclic methylene bonds; the characteristic molecular markers at 3080, 1645, 841 and 697 cm^{-1} for these structures

do not appear in the spectra of dragon's blood specimens studied here.

Finally, the dragon's blood *Dracaena draco* L. resin specimen from Socotra gave a very inferior quality Raman spectrum (Fig. 7) compared with those from the same botanical species from other geographical locations and with the *Dracaena cinnabari* specimen also from a Socotran source (Fig. 5). The Socotran specimen of *Dracaena draco* is unlike anything else attributed here to dragon's

Table 2
Vibrational wavenumbers (in cm^{-1}) and assignments in the Raman spectra of 'Dragon's blood resins' from several sources

<i>Dracaena cinnabari</i> (resin bead)	<i>Daemonorops draco</i> (powder)	<i>Eucalyptus terminalis</i> (resin fragment)	Approximate assignment of vibrational mode
3062 m	3063 w	3064 m 3054 w	v(CH) olefinic v(CH) olefinic
3011 mw			v(CH) aromatic
2937 mw, br	2931 mw, br 2869 mw, br	2933 mw, br	v(CH ₃) symmetric v(CH ₂) symmetric
2850 mw, br		2859 w	v(CH ₂) symmetric
	2715 vw		v(CCH) aliphatic
1662 m, sh	1660 vw	1689 mw	v(C=O)
		1614 s	v(C=C)+v(C=O)
1604 ms	1600 m		v(C=C)+v(C=O)
1575 mw, sh			v(C=C)+v(C=O)
	1545 w		v(C=C) aromatic ring
1539 m			v(C=C)
1515 w, sh	1511 m		v(C=C)
1445 mw, br	1451 mw	1449 vw 1428 mw	v(C=C)+v(C-O)+ δ (CCH) v (C=C)+v(C-O)+ δ (CCH)
1392 w	1390 w		δ (CH ₂)
		1367 mw, br	δ (CH ₂)
	1356 mw		δ (CH ₂)
1343 mw	1340 w		δ (CH ₂)
1300 m, br		1291 mw	δ (CH ₂)
	1265 w		v(C-O)+v(C-C)
1254 mw			v (C-O)+v(C-C)
1211 m		1205 mw	v(C-O)+ δ (CCH)+ δ (ring)
	1190 w, br		v (C-C)
1171 m			v (C-C)
1112		1104 w	v (C-C)
1035 w, br			v(C-C)+v(C-O)
	1001 mw, sharp	1001 mw, sharp 973 w	v(CC) aromatic ring
955 w			ρ (CH ₃)
891 vw			ρ (CH ₃)
		862 vw	ω (CH)
847 m	840 vw, br		ρ (CH ₂)
830 w, sh			δ (CCH) aromatic
	800 w		δ (CCH)
		780 ms	δ (CCH)
736 m, br			v(CC)
690 w			ω (C-O)+ ω (C=O)
670 w			δ (CCC) aromatic
641 m		640 mw	δ (CCC) aromatic
		590 w	δ (COC)
		548 w	δ (COC)
	480 mw		δ (CCC)
410 w			δ (CCC)

blood resin; in fact, the spectrum has only two bands, at 1001 and 1600 cm^{-1} , which are assignable to the resins we have studied here with a relative band intensity similar to *Daemonorops draco*. However, other weaker features, which could have assisted in the classification of this resin botanical source are lost in the higher background noise in this spectrum. Since this resin specimen was harvested botanically and not purchased commercially, synthetic or processed formulations resulting in chemical degradation may be discounted as an explanation of the poorer spectral quality. It can be stated that from the Raman spectrum, it is unlikely that this resin specimen is a sample of *Dracaena draco*, as demonstrated by the specimens examined in this work.

An example of the Raman analysis of a 'false' dragon's blood resin is provided by a deep blood-red coloured material obtained from a market in Al Kuri, Aden, the spectrum of which is shown in Fig. 8. Clearly, there are no bands assignable to the *Dracaena* and *Daemonorops* dragon's blood resins analyzed earlier; the spectrum in Fig. 8 is assignable to calcite, with Raman bands at 1087, 715, 284 and 156 cm^{-1} , aragonite (the marine seashell form of calcium carbonate with a carbonate stretching mode at 1019 cm^{-1}) and carotene [28] with a C=C and a C–C bands at 1525 and 1155 cm^{-1} , respectively. The weaker Raman bands at 1750 and 1440 cm^{-1} are not assignable with any certainty but they could be an ester or gum which has been used to incorporate or bind the material together, or to calcite–aragonite. Hence, this specimen is definitely not a dragon's blood resin and is better described as a red coral base with perhaps added calcium carbonate and a gum binder.

3. Conclusions

The FT-Raman technique is capable of distinguishing between freshly harvested resins from *Dracaena cinnabari*, *Daemonorops draco*, *Dracaena draco* and *Eucalyptus terminalis* trees, all

of which are known as dragon's blood. The small amount of sample required for the analysis is important for the identification of the resins applied to artefacts and for the conservation of objects in museum collections. Although the resins studied here are of nearly identical color and appearance, and have similar behavior dissolution in solvents, they are of somewhat different chemical composition. The current work represents a stage in the evaluation of Raman spectroscopy as a nondestructive analytical technique for the examination of resins of importance in antiquity, and is a step forward in the construction of a spectroscopic database of resins, gums, waxes and biomaterials for the archaeological and forensic study of degradation and survivability of sensitive material in different burial environments. An understanding of the degradation of, for example C=C bonds and C=O bonds, as sites of reactivity in vulnerable materials is essential for the preservation of sensitive artefacts. Also, as has been demonstrated here, the Raman spectrum has features which when modified can point towards the pretreatment or processing of resins and pigments, and can indicate valuable information for archaeologists about the extent to which materials were subjected to simple technological treatment in early cultures. As a result of this work, the key molecular biomarker bands of dragon's blood are identified in the region 1400–1700 cm^{-1} , depending on the botanical source.

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