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# Identification of resinous materials on 16th and 17th century reverse-glass objects by gas chromatography/mass spectrometry

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ABSTRACT

Objects of *hinterglasmalerei*, reverse-glass paintings, are painted on the back side of glass panels. Obviously, the paint layers are applied in reverse order, starting with the uppermost layer. The finished *hinterglas* painting is viewed through the glass, thus revealing an impressive gloss and depth of colour. The binding media of two precious objects of *hinterglasmalerei* from the 16th and 17th century have been identified as almost exclusively resinous. Identification was performed by a special optimised analysis procedure, which is discussed in this paper: solvent extracts are analysed by gas chromatography/mass spectrometry, both with and without derivatisation or hydrolysis. In an additional step, oxalic acid is added to the methanol extracts prior to injection. This attenuates the peaks of the non-acidic compounds, whereas the acids elute with good resolution. The non-acidic compounds are emphasised after injection of the underivatised extracts. This approach minimises compositional changes caused by the sample preparation and derivatisation steps. Chromatograms of aged samples with a very complex composition are simplified, which allows a more reliable and straightforward identification of significant markers for various materials. The binding media of the *hinterglas* objects were thus shown to consist of mixtures of different natural resins, larch turpentine, heat-treated *Pinaceae* resin or mastic. Typical compounds of dragon's blood, a natural red resin, were also detectable in red glazes by the applied analysis routine. Identification of the binding media provides valuable information that can be used in the development of an adequate conservation treatment.



## 1. Introduction

Different mass spectrometry techniques are widely used in modern scientific research, but only a rather small number of laboratories are working with MS in the field of cultural heritage. Gas chromatography in combination with mass spectrometry (GC/MS) is a powerful tool for the characterisation and identification of organic binding media used on works of art. This article presents investigations of two objects painted in *hinterglasmalerei* (reverse-glass technique) [1–3]: a Southern German house altar (The Corning Museum of Glass, New York, Figs. 1–3), dating probably around 1560–1580, and a game box (Dresdener Kunstkammer, Germany, Figs. 4 and 5), dating around 1680 [4]. In contrast to conventional paintings, a glass panel is used as a support for *hinterglasmalerei*. The paint layers are then applied to the back side in reverse order, starting with the foreground and working 'backwards'. However, not only glass, but all kinds of transparent materials can be used as the support. In our two examples, glass was used for the Corning house altar, whereas amber was used for the Dresden game box.

*Hinterglas* objects as precious as the Corning house altar and the Dresden game box are rare and have hardly ever been investigated for the use of materials. With respect to the binding media, available information from historic sources is very general and mentions the use of oils, proteins and resins [5,6]. Optimised analytical procedures, including standardised preparation and investigation methods, are essential to identify complex mixtures in very small samples. The compositional complexity is further increased by ageing and degradation processes. There may be additional contamination with more recent restoration and conservation materials. In art technological examinations, the aim is to identify the main components that serve as characteristic markers for specific materials. This approach allows differentiation between similar materials, and permits linking with marketed product names. The analysis of reference materials of precisely defined botanical origin and the characterisation of particular biomarkers or degradation markers will provide useful tools for the analyst.

Binding media analyses of *hinterglas* objects are very rare [7]. In the course of ongoing research projects on *hinterglasmalerei*,

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**Fig. 1.** The small house altar (approximately 1560–1580), attributed to Southern Germany (perhaps Nuremberg or Augsburg), after restoration. The Corning Museum of Glass (59.3.39), height 49.6 cm; width (closed wings) 19.5 cm; depth 12.7 cm. ©The Corning Museum of Glass, Corning (NY).

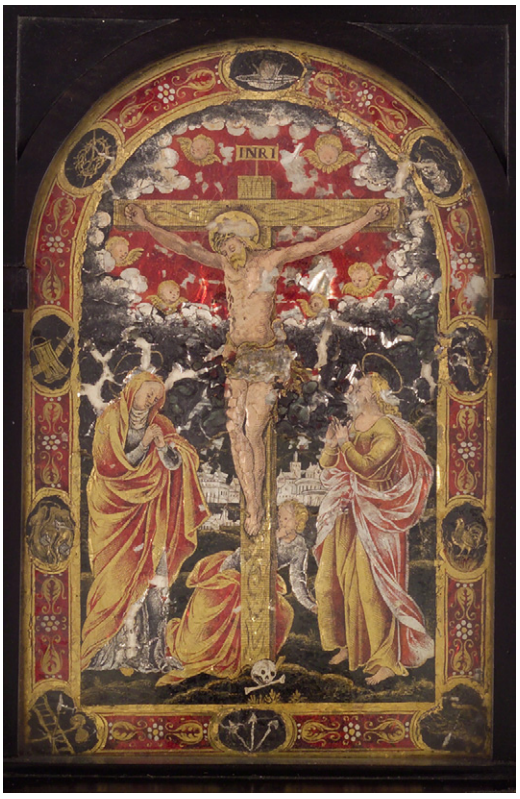


**Fig. 2.** Corning house altar, central panel 'Crucifixion' before restoration. White paint losses due to delamination from the glass can be seen in the discoloured black (formerly blue) areas, as well as in the red area around the cross. Partial delamination also explains the greyish structures in the black paint (cf. Fig. 1). ©The Corning Museum of Glass, Corning (NY).

**Fig. 3.** Corning house altar, detail of 'Virgin as Queen of Heaven'. Behind the glass support, a metal leaf is applied, etched with a needle or stylus and covered with a layer of colourful translucent glaze (*amelierung* technique). Delamination, cupping and losses of the aged binding medium are clearly visible. ©Simone Bretz, Munich.

binding media of objects dating from the 14th to 19th century were analysed. In accordance with the historic sources, a broad variety of binding media were identified (unpublished results). In this article, we focus on the analysis of resinous binding media and the discrimination of resins from different botanical sources. An optimised analytical procedure is presented and applied to a selection of resins. To demonstrate the applicability of the procedure to real objects, two case studies of *hinterglas* objects were selected on the basis of their resinous binding media. The aim of the research presented here is to further our understanding of historical manufacturing techniques and to provide deeper insights into some of the degradation processes that lead to delamination and paint flaking (Figs. 2 and 3). Additionally, accurate identification of the binding material can assist in the conservation and preservation of precious art objects.

## 2. Experimental

### 2.1. Gas chromatography/mass spectrometry (GC/MS)

GC/MS analysis was performed using a gas chromatograph of the HP 5890 series II (Hewlett-Packard/Agilent) coupled to a Hewlett-Packard quadrupole mass spectrometer type 5989B, MS Engine, in the electron impact (EI) mode, scan range 40–500 $m/z$. The chromatograph was equipped with a DB-5ht column (J&W,

**Fig. 4.** The folding game box decorated with amber was transferred to the Dresden Kunstkammer in the year 1687 (inv.-no. RK P 358). The image shows the open box with the decorated trictrac board. Dimensions (closed): 21 cm × 21 cm, height 8 cm. ©Staatliche Kunstsammlungen Dresden, Grünes Gewölbe, Dr. Martina Minning.

5%-phenyl-methyl-polysiloxane), 30 m, 0.25 mm ID, 0.1 μm film thickness. Measurement conditions: carrier gas Helium 5.0 (purified), constant-flow mode, 1.7 ml/min; split/splitless injector: injection temperature = 250 °C, splitless mode, 1–2 μl injection volume, 0.5 min splitless; purge flow 36 ml/min; oven program: T1 = 55 °C, t1 = 1 min, R1 = 15 °C/min, T2 = 150 °C, R2 = 10 °C/min, T3 = 360 °C; NIST library, version 05.

### 2.2. Sample treatment

Samples of 0.2–0.5 mg were pre-treated for GC/MS by step-wise extraction with different solvents (isooctane, methanol, chloroform/methanol [7:3, v/v], anhydrous oxalic acid in methanol [10%, w/v]), all chromatographic grade (Merck chemicals, D-64293 Darmstadt). The extracts were injected without derivatisation. Anhydrous oxalic acid (puriss, Fluka, CH-9471 Buchs SG) was added to the methanol extract of some samples prior to injection. Methylation with trimethyl sulfonium hydroxide (TMSH, 0.2 M in methanol, Macherey-Nagel, D-52355 Düren) was also used: the samples were mixed with TMSH solution and heated (approximately 30 min, 50 °C) in a closed sample vial for methylation/transesterification [8].

**Fig. 5.** Detail of the Dresden game box, showing red, green and black ornaments in *hinterglasmalerei* on the back of originally clear amber pieces. Today the colouring is obscured by the yellowed and browned amber. ©Annina Seele, Heidelberg.

### 2.3. Reference materials

The Doerner Institut houses a large collection of natural resins and colourants of modern and historic origin that were used as reference materials in this study. The collection includes commercial materials as well as samples of defined botanical origin. Mastic resin was collected on the island of Chios, Greece [9], and larch turpentine was obtained directly from a producer in Tyrol [10]. Dragon's blood was obtained from various sources in the producing countries by Katja Lewerentz [11]. Generally, resins and colourants from the Martius Botanical Collection (dating around 1825–1863) were used in the study [12].

## 3. Application of GC/MS to the analysis of resinous materials in aged art objects

The following paragraphs will focus on the differentiation of natural resins that were found in the two *hinterglas* objects. An optimised analytical approach is presented along with a discussion of the main markers of selected resins (larch turpentine, *Pinaceae* resin, mastic, and dragon's blood, a red plant resin).

### 3.1. Optimised analytical procedure

Owing to the enormous complexity of aged and altered materials, a special solvent extraction scheme is usually applied prior to analysis [13]. With the help of solvents of differing polarity, diverse material groups can be separated and complex mixtures respectively chromatograms can be unravelled, thus allowing a more clear and unambiguous identification of the materials. However, because most of the characteristic markers of aged resins are soluble in methanol, no further simplification of the chromatograms can be achieved by solvent extraction. Instead, a special procedure (Fig. 6) proved useful for resinous mixtures because it allows separate detection of non-acidic and acidic compounds [13]. This can easily be achieved if the methanol extract is first injected without further derivatisation and again after the addition of approximately 10% (w/v) anhydrous oxalic acid to the methanol. Without derivatisation, the non-acidic compounds dominate the gas chromatogram because the acidic compounds are not properly separated by the non-polar column and their peaks are attenuated. After co-injection of oxalic acid, the chromatographic behaviour is inverted and the acidic compounds

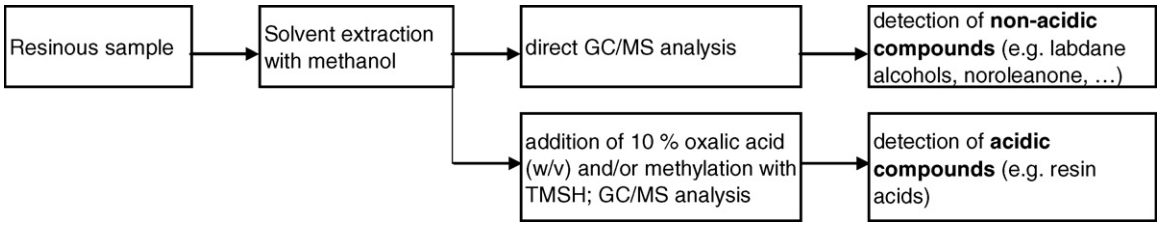


**Fig. 6.** Scheme of the analytical approach used for the identification of resinous binding media.

dominate the chromatogram because they are abundant in most resins and are now well resolved, even without derivatisation (methylation). Presumably, the added oxalic acid occupies all the active sites (metal oxides, siliceous groups) in the injector and the column of the GC/MS. This might prevent the diterpenoid resin acids from being absorbed and retained in the sites already occupied by the stronger oxalic acid. At the same time, the polarity of the separation column seems to undergo a short-term shift towards the polar range to the extent that the polar resin acids are now able to interact with the stationary phase and can thus be separated.

For resins, the use of oxalic acid in addition to conventional derivatisation (methylation or silylation) has several advantages: firstly, methylated resin acids can be original compounds in samples that may give valuable hints on the production or origin of the materials [14]. Secondly, the chromatograms are less complicated because the peaks of non-acidic compounds are attenuated. Thirdly, the composition of the sample is not altered by the derivatisation process, which is crucial as it has long been known that abietane-type acids, in particular, can isomerise under acidic conditions or on heating [15–17]. Additionally, if the resins are generally derivatised prior to analysis, the gas chromatograms are dominated by the resin acid esters. Unfortunately, most of these acids are very unspecific and are found in many resins [18,19]. Identification is therefore hampered because more specific components can be overlooked or hidden in resin mixtures of complex and aged art objects. This is especially true for sandarac and larch turpentine because their very specific non-acidic markers allow identification even in low concentrations (see Section 3.2). Derivatisation with tetramethylammonium hydroxide (TMAH, a strong basic catalyst), often in combination with pyrolysis, can reduce important non-acidic markers by hydrolysis and formation of side products, which complicates identification of the resins [17,20].

The analytical approach described here does not provide a comprehensive total chemical analysis of a sample. Instead it is optimised to identify specific patterns and marker compounds that lead to the identification of bulk materials that were used by the artist. Thus, materials of similar composition, e.g., similar resins, can be distinguished in mixtures, and treatments during the manufacturing process, e.g., thermal treatments, can be demonstrated even in the aged samples (see Sections 4.1 and 4.2).

### 3.2. Identification of larch turpentine

The balsamic larch turpentine originates from *Larix* species (*Larix decidua* Mill.), which is native to Europe, especially in the Tyrolean region of Austria. Larch turpentine belongs to the group of 'fine turpentines'. It does not have a tendency to crystallise and retains a long-lasting elasticity [21]. Larch turpentine has always been expensive due to its low yields and labour-intensive tapping methods [22]. Tyrolean larch turpentine was also named 'Venetian turpentine' on account of the fact that it has been traded via Venice. However, this trade name often leads to misunderstandings because 'Venetian turpentine' was often a mixture of larch turpentine with colophony [23]. Thus, for reference analyses, only clearly defined material should be used, if possible directly from a producer (see Section 2.3).

Larch turpentine can easily be identified by GC/MS in both fresh and aged resin mixtures by means of the non-acidic labdane alcohols – epimanool, larixol and larixyl acetate [22,24] – in the methanol extract without derivatisation. Epimanool has a characteristic mass spectrum (Table 1), but its enantiomer (manool) also occurs in other natural resins (e.g., sandarac). In contrast, larixol and larixyl acetate are clear and characteristic markers for larch turpentine (Table 1); however, both components are sensitive to alterations and also react very sensitively with aggressive derivatisation agents, as described above [18,20].

In addition to non-acidic diterpenoids, larch turpentine also contains acidic compounds [19,25], but because alterations of

**Table 1**
Characteristic markers of larch turpentine (L1, L2, L3), aged and oxidised *Pinaceae* resin (DA, ODA, ODDA) and mastic (M).

| Trivial name | Abbreviation | Formula | MW | 10 most abundant peaks |
|---|---|---|---|---|
| Epimanool | L1 | $C_{20}H_{34}O$ | 290 | 137 (100), 81 (68), 95 (59), 69 (48), 41 (48), 93 (43), 43 (42), 55 (42), 71 (41), 123 (36) |
| Larixol | L2 | $C_{20}H_{34}O_2$ | 306 | 69 (100), 109 (93), 95 (67), 153 (64), 81 (62), 93 (58), 71 (57), 55 (50), 107 (46), 43 (46) |
| Larixyl acetate | L3 | $C_{22}H_{36}O_3$ | 348 | 153 (100), 255 (77), 43 (75), 69 (58), 95 (54), 123 (54), 105 (51), 119 (49), 81 (46), 93 (45) |
| Dehydroabietic acid | DA | $C_{20}H_{28}O_2$ | 300 | 285 (100), 239 (95), 300 (29), 197 (27), 286 (21), 240 (20), 254 (17), 141 (15), 43 (12), 129 (11) |
| 7-Oxo-dehydroabietic acid | ODA | $C_{20}H_{26}O_3$ | 314 | 253 (100), 314 (43), 211 (28), 299 (23), 43 (21), 254 (21), 239 (16), 285 (14), 300 (12), 213 (11) |
| 7-Oxo-dehydro-dehydroabietic acid | ODDA | $C_{20}H_{24}O_3$ | 312 | 251 (100), 312 (49), 253 (37), 211 (21), 314 (21), 252 (20), 43 (14), 197 (13), 313 (12), 299 (11) |
| 28-Norolean-17-en-3-one | M | $C_{29}H_{46}O$ | 410 | 163 (100), 191 (56), 190 (20), 410 (15), 164 (14), 192 (11), 119 (9), 121 (9), 189 (9), 205 (6) |

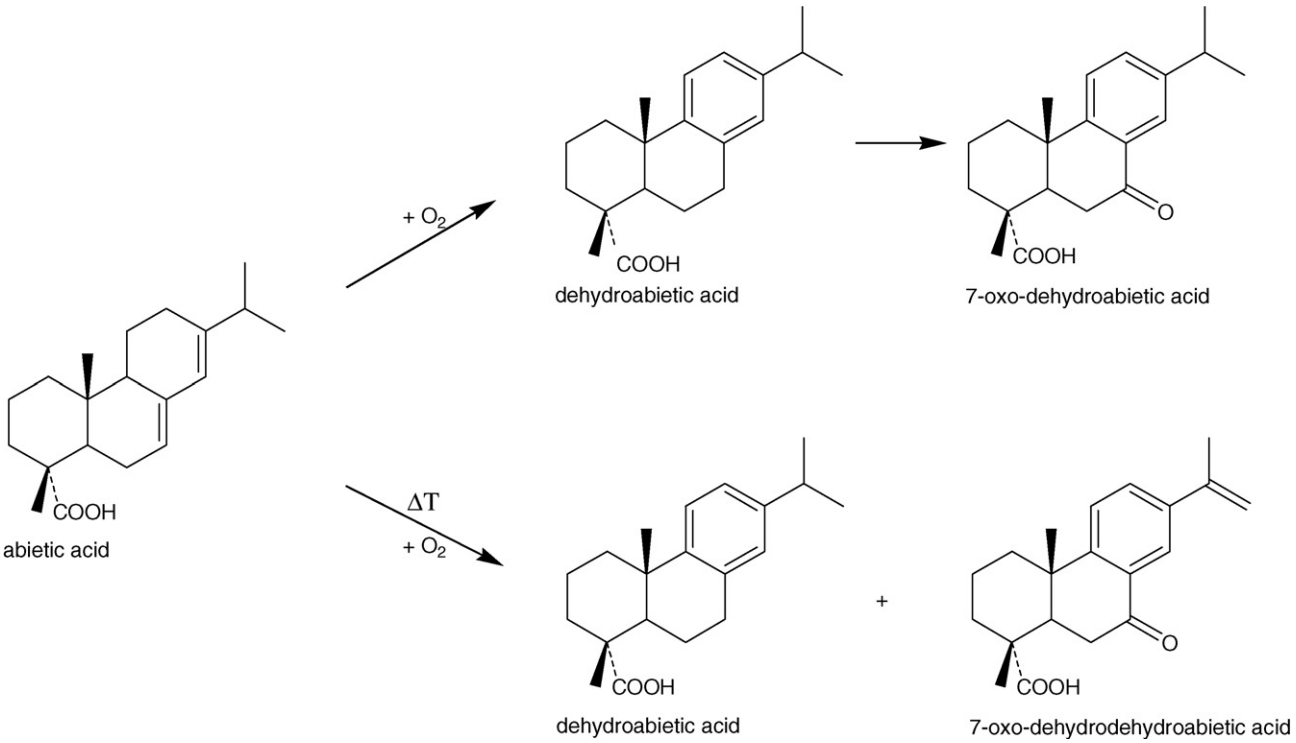


**Fig. 7.** Abietane-type molecules with conjugated double bonds (abietadienic acids) easily undergo isomerisation and oxidation reactions. Dehydroabietic acid (DA) is readily formed during ageing, but further dehydrated products (e.g., ODDA) are indicative of extensive heating.

larch turpentine with colophony are quite frequent (trade product 'Venice turpentine'), we strongly recommend the identification method based on non-acidic compounds instead of resin acids.

### 3.3. Identification of Pinaceae resin

In addition to the 'fine turpentines', which are naturally clear, pale and light yellow balsamic resins, 'common turpentines' are also known. These common turpentines include the balsamic resins of a large number of pine species and spruce. The common turpentines are produced by resin tapping. The principle of resin tapping is basically the same throughout all species, the natural flow of resin is increased by removing the bark [21].

Diterpenoid resin acids of the abietane type are the most abundant components of natural diterpenoid resins from the *Pinaceae* family. Their resins are usually distilled to obtain oil of turpentine, and the solid residue is called colophony. Isomerisation and disproportionation reactions during the distillation process produce abietic and particularly dehydroabietic acid (DA) from a varying number of diterpene resin acids [15]. On prolonged exposure to air and light (or heat), the resulting – relatively stable – dehydroabietic acid will oxidise and produce several oxidised products (Fig. 7 and Table 1) [26–29]. Large amounts of abietic acid derivatives are therefore indicative of *Pinaceae* resin. This is especially true if additional compounds are present that do not develop from normal (autoxidative) ageing, but from thermal treatments, e.g., dehydrodehydroabietic acid[1] or 7-oxo-dehydrodehydroabietic acid (Fig. 7). These compounds can be identified in the methanol extract with added oxalic acid.

[1] It was not possible to distinguish between 6-dehydrodehydroabietic acid or 15-dehydrodehydroabietic acid.

### 3.4. Identification of mastic

Mastic is the resin of the mastic tree (*Pistacia lentiscus* L.) of the pistachio family. The branched evergreen shrub reaches heights of between four and six metres. The resin has been obtained since ancient times mainly from the sub-species *Pistacia lentiscus* L. *var chia* DC., cultivated on the southern half of the Greek island of Chios, although the genus *Pistacia* (family Anacardiaceae) contains some 10–15 species. Most of them occur naturally in the Mediterranean and neighbouring areas.

Mastic is a triterpenoid resin, in contrast to *Pinaceae* resins and larch turpentine. Fresh mastic resin dissolves in alcohol and shows characteristic markers in the non-acidic fraction. The most useful non-acidic marker for mastic resin is 28-norolean-17-en-3-one (Table 1). It is an important ingredient in all mastic samples analysed and does not alter with time, a fact which accounts for its usefulness in the analysis of mastic. Furthermore, it possesses a highly characteristic mass spectrum and is absent from other natural triterpenoid resins such as dammar and elemi that are often found in admixture with mastic. Triterpenoid acidic marker compounds are also found after methylation (e.g., with TMSH) of the mastic resin [30], but the non-acidic fraction already suffices for a reliable identification of the mastic resin source.

### 3.5. Identification of dragon's blood

Within the described extraction scheme, not only resinous components from transparent glazes were detected, but also different sorts of dragon's blood were identified and distinguished by characteristic markers. Dragon's blood is a common non-specific name for red-coloured plant resins [11] and not a denotation for a single product from only one plant or tree (like mastic or larch turpentine). Nowadays, two main plant families (*Dracaena* and *Daemonorops*) deliver the red resin [31]. *Dracaena* plants are related to

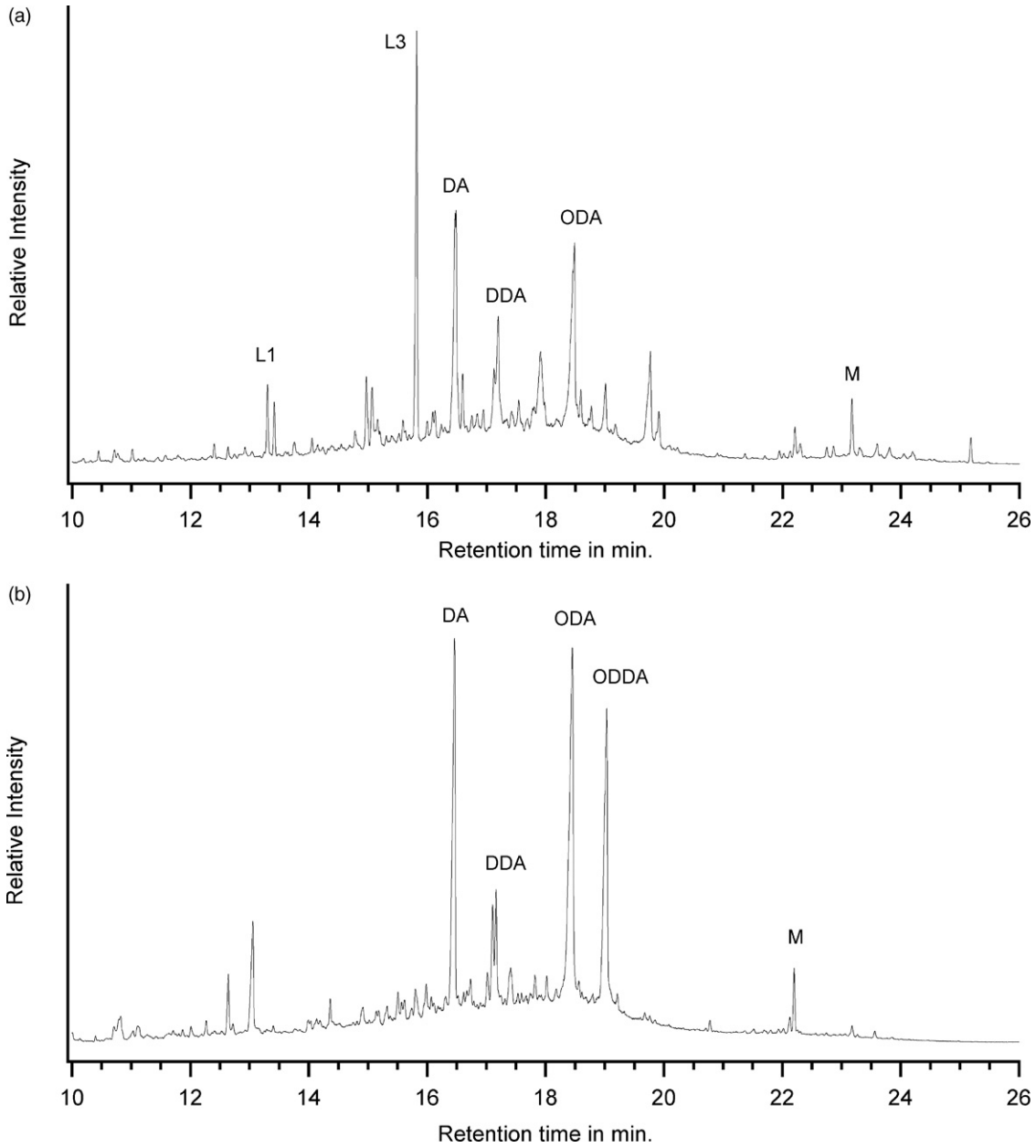


**Fig. 8.** Red glaze from the St. Prigida panel of the Corning house altar: gas chromatograms of the pure methanol extract (a) without and (b) with addition of 10% anhydrous oxalic acid. In the underivatised methanol extract (a) the non-acidic labdane alcohols from larch turpentine show good resolution (L1 and L3). Due to the polarity change of the column after the addition of oxalic acid (b) the main components of the sample, the resin acids from heat-treated *Pinaceae* resin, are detectable (DA, ODA, ODDA). The signals of non-acidic compounds (e.g., L3) are now completely attenuated, which simplifies the chromatograms.

the *agave* and *lily* genus and grow in tropical/sub-tropical Africa, Asia and Australia. Only a few species deliver the red resin called dragon's blood; these are mainly *Dracaena draco* L. and *Dracaena cinnabari* BALF. fil. The *Daemonorops* family comprises over 115 known species, most of which are native to India, South China and the Malay Archipelago. In contrast to *Dracaena*, the *Daemonorops* species belong to the family of *palmae*. The most common dragon's blood – containing the typical component Dracorhodin – originates from the *Daemonorops draco* species, but other resin-delivering species (such as *Daemonorops micracantha*) are known.

**Table 2**
Analysis results of the Corning house altar glazes.

| Corning house altar | Main components | Minor components | Colouring agent |
|---|---|---|---|
| Red glaze | Heat-treated *Pinaceae* resin, larch turpentine | Mastic, camphor, spike oil | Cochineal[a], dragon's blood[b] |
| Green glaze | Heat-treated *Pinaceae* resin, larch turpentine | Mastic, camphor, spike oil | 'Copper green'[c] |
| Blue paint | Heat-treated *Pinaceae* resin, larch turpentine | Mastic, spike oil, egg | Smalt[c] |

[a] Determined by HPLC.
[b] Determined by GC/MS.
[c] Determined by SEM-EDX.

Usually, red lakes and dyestuffs are routinely analysed with TLC [31] or HPLC methods [32], but the *Daemonorops draco* and *D. micracantha* species also show characteristic markers with GC/MS. Analysis of reference material from the *D. draco* species reveals that it contains some compounds with rather high molecular weight, such as Dracorubin (MW 488 Da [19]), as well as the flavonoid Dracorhodin (anhydro-7-hydroxy-5-methoxy-6-methy-2-phenyl-benzopyranol, MW 266 [33]). The latter shows a typical mass spectrum (Appendix A). In many reference samples of *D. draco*, including some of the Martius collection from the 19th century, additional triterpenes were found [34] that reveal similarity with dammar.

The precisely characterised botanical reference material enabled the characterisation of two marker compounds of the red plant resin from *D. micracantha* (Griff.) *Becc* (Appendix A). No precise formula or molecular weight could be attributed up to now. A sample of dragon's blood in the Martius collection revealed identical mass spectra. We therefore conclude that resins from *D. micracantha* species – similar to other *Daemonorops* resins growing in the Malay region – have been traded under the name of dragon's blood since historic times.

## 4. Results of the two *hinterglasmalerei* case studies

All samples of the reverse-glass paintings of Corning and Dresden showed a very good solubility in alcohol during extraction. This is usually a strong indication of primarily resinous binding media, which was confirmed by the analysis of these objects. In contrast to the small number of binding media analyses [7] and the literature on the binding media of reverse-glass paintings [5,6], no drying oils were identified in the samples.

### 4.1. Case study of the Corning altar

The analytical procedure discussed in Section 3.1 was applied to identify the binding media of the *hinterglas* altar from The Corning Museum of Glass. The glazes studied (red, red-brown, green and blue) showed a very good solubility in alcohol and the gas chromatographic/mass spectrometric analyses revealed mainly resinous compounds in all samples, with only slight variations in the quantitative composition.

The main components in all samples were diterpenoid resin acids of the abietane type, especially dehydroabietic acid and its oxidation and dehydrogenation products, 7-oxo-dehydroabietic acid (ODA) and 7-oxo-dehydrodehydroabietic acid (ODDA). As already mentioned, large amounts of abietane-type acids are typical of *Pinaceae* resins. However, the resin used in the Corning altar is not only aged and oxidised, but also reveals large amounts of a dehydrogenated resin acid (ODDA). This compound is not a typical oxidation product and usually only develops in large quantities if the resin was strongly heated [35]. Similar compounds are also known from melting-out processes of resinous wood in tar production [36]. However, methyl esters, which are characteristic for the presence of wood during heating, were absent. The main components now present in the Corning samples are therefore the degradation and heating products that resulted exclusively from the *Pinaceae* resin, probably pine resin (Table 1).

With the help of our extraction scheme, non-acidic diterpenoid components were also identified in the translucent glazes (L1, L3, see Section 3.2), which originate from larch turpentine. In the methanol extract of the red glaze, the biggest peaks are attributed to the labdane alcohols of larch turpentine (Fig. 8a). The chromatographic response of the non-acidic components is extremely high in this case, whereas the huge amounts of resin acids from the heat-treated *Pinaceae* resin are recognisable when the acidified methanol extract is injected (Fig. 8b).

A third resin was identified in the triterpenoid region of the chromatogram. Small amounts of noroleanenone (M) and other related oleanane-type structures were detected, which are typical compounds of aged mastic (see Section 3.4).

A special highlight was the identification of dragon's blood in two red glazes. Dragon's blood is often mentioned in historical recipes (e.g., Ref. [5], p. 367), but only very few analytical proofs are known owing to the diversity of the materials. In the methanol extract of the red glazes of the Corning house altar, the typical mass spectra of Dracorhodin (Appendix A) accompanied by specific triterpenes with mainly dammarane structures were identified by

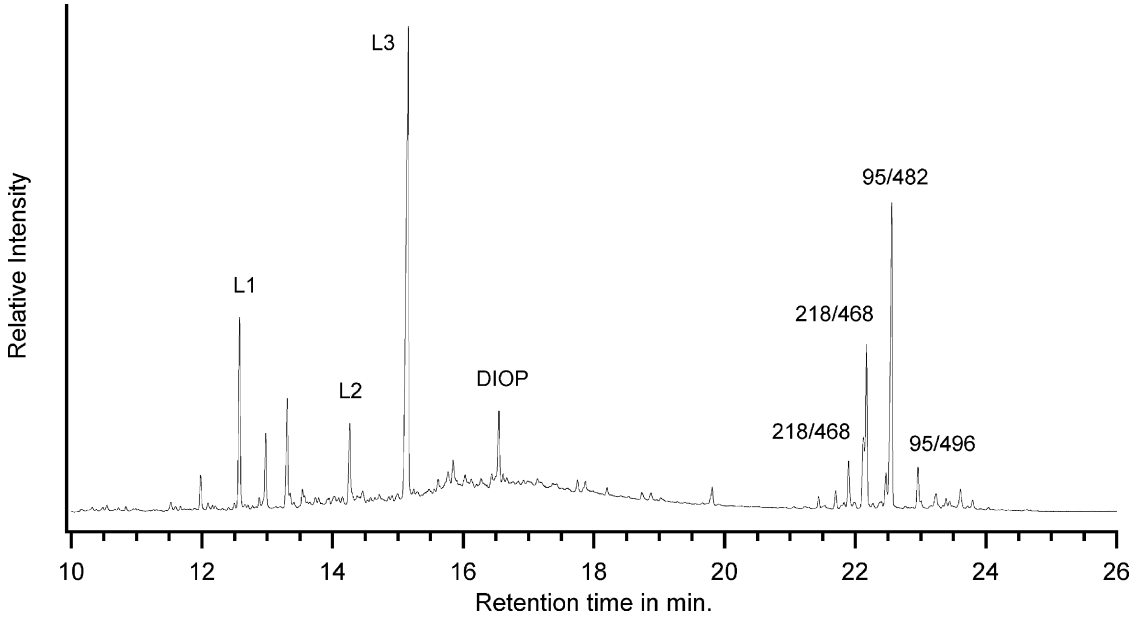


**Fig. 9.** Red glaze from the amber game box, gas chromatogram of the methanol extract. Markers of larch turpentine are clearly visible (L1, L2, L3). The origin of the triterpenoid compounds at 21–24 min is unclear (labels: base peak/possible molecular weight). The presence of modern plasticizer (phthalate ester) in one sample indicates a modern restoration treatment.

**Table 3**
Analysis results of the Dresden game box glazes.

| Amber game box | Main components | Minor components | Colouring agent[a] |
|---|---|---|---|
| Red glaze (sample I) | Larch turpentine, triterpenoids (unknown) | Modern plasticizer (diisooctylphthalate, DIOP) | Dragon's blood |
| Red glaze (sample II) | Larch turpentine | | Dragon's blood |

[a] Determined by GC/MS.

GC/MS. These compounds are typical of *Daemonorops draco* palmae (see Section 3.5).

The employed resin mixture is thus composed of Southern German materials (*Pinaceae* resin, larch turpentine) along with imported resins (mastic, dragon's blood). In addition to the resinous binding media, other components were found that cannot be discussed in too much detail here: remains of the initial solvent (spike oil) are recognisable by monoterpenoids that are not contained in the identified resins, and other monoterpenoids were added as natural softeners (camphor) [37]. In the red glazes, dyes from a red lake (cochineal) were detected by HPLC in addition to the dragon's blood. In the blue paint, smalt was found by SEM/EDX, and egg binding medium by amino acid analysis [38]. A summary of the identified materials is given in Table 2.

### 4.2. Case study of the amber game box

We were able to analyse the Dresden game box during its conservation. This included two nearly untouched samples of red glazes [4]. The GC/MS results show larch turpentine as the main component in both samples (Fig. 9 and Table 3). Typical markers of *Pinaceae* resin or mastic were missing. In the non-derivatised methanol extract, additional compounds of a dragon's blood species (*D. micracantha* (Griff.) *Becc*) were determined with GC/MS (Appendix A). Similar to the better known *Daemonorops draco* palmae, this *D. micracantha* species delivers a bright-red resin as well.

Owing to discolouration of the amber, the game box appears mainly reddish brown today (see Figs. 4 and 5), but the original appearance – now only visible from the back side – was more colourful and lustrous because the pieces of amber were all clear and light yellow initially. An indication that the colours of the glazes were also more diverse than visible today is provided by the triterpenoids, which are only contained in one red glaze (Fig. 9, and Table 3 sample I), thus at least two differing red glazes were applied. According to the mass spectra, the main triterpenoids have molecular weights of 468 and 482 Da (Appendix B). Unfortunately, the mass spectra do not allow an unambiguous identification of the compounds because α- and β-amyrin acetates and derivatives of boswellic or commic acids give very similar spectra. Boswellic acids are contained in frankincense, commic acids in myrrh, and amyrins in elemi and other resins that are known to be components of historical lacquers and glazes [39,40]. However, similar compounds are found in many other plants, and dragon's blood may also contain similar triterpenoids as accompanying products [41].

## 5. Conclusions

The binding media of two precious *hinterglasmalerei* objects, a house altar of the 16th century and a game box of the 17th century, were identified by GC/MS. An optimised analysis procedure was applied that consists of extracting with solvents and injecting underivatised samples as well as admixtures with oxalic acid. Even in small and aged samples, mixtures of several different resins and colouring agents were identified. The translucent coloured glazes of the house altar consist of larch turpentine, heat-treated *Pinaceae* species (probably pine resin) and mastic. The red glazes on the game box mainly consist of larch turpentine. In all investigated red samples, the admixture of red dyestuffs was demonstrated. So-called dragon's blood – a general term for red plant resins – seems to be an important ingredient in translucent red glazes. With the help of GC/MS, at least two different *Daemonorops* species were identified as the colouring agent.

The most typical disfigurement that occurs in reverse paintings on glass is the separation of paint from the glass. When viewed from the front, such damage appears as patches of greyish, less saturated areas of paint because light is scattered on the surface structures that are introduced by the delamination (Figs. 2 and 3). The identified resins, larch turpentine, mastic and also *Pinaceae* resins, are therefore ideal binding media for *hinterglas* objects because they are 'soft' resins that are elastic to some extent. 'Hard' resins, such as sandarac [42] or amber, were accordingly not used as they would be too inelastic, although they are mentioned in historic recipes ([5], pp. 352, 353). Nevertheless, in both case studies presented here, the resin binding media have become brittle due to ageing and oxidation of the resins.

Owing to the fact that there are many different types of *hinterglasmalerei*, each reverse-painted glass will require an individual approach to its treatment. For the conservation of the Corning house altar it was especially important that the alcohol-soluble resin paint layers were treated with adequate, i.e., non-polar and non-oxidisable glueing materials (Regalrez 1094 and TeCerowax 30445) that could be applied in non-polar solvents without dissolving the resins. The former transparency, gloss and brilliant saturation of the original glazes were re-established, especially on the Corning house altar.

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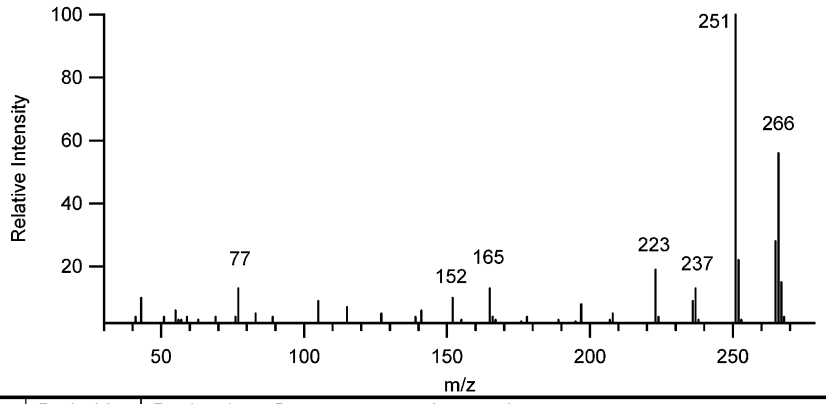
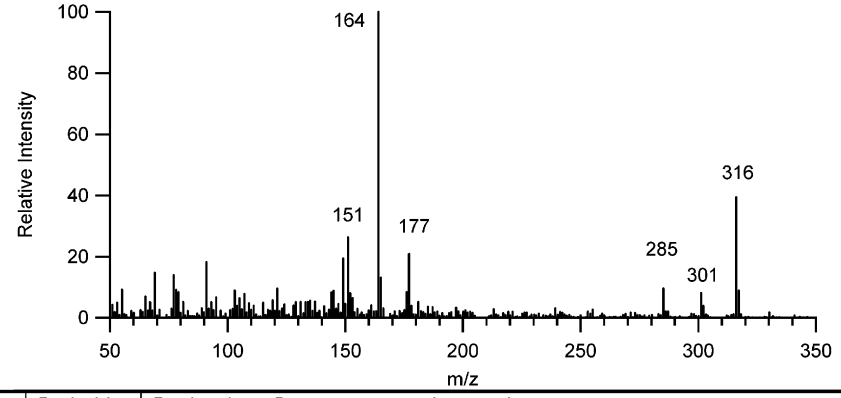
## Appendix A

Mass spectra of different dragon's blood components in the red glazes of the Corning house altar (Dracorhodin) and the amber game box (peaks 1 and 2).

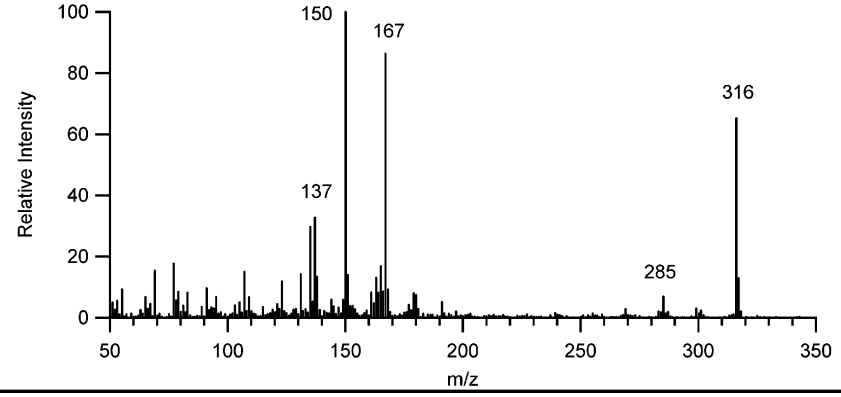
| Formula | MW | Trivial name |
|---|---|---|
| $C_{17}H_{14}O_3$ | 266 | Dracorhodin from Daemonorops draco |




| ? | Probably 316 | Peak 1 from Daemonorops micracantha |
|---|---|---|



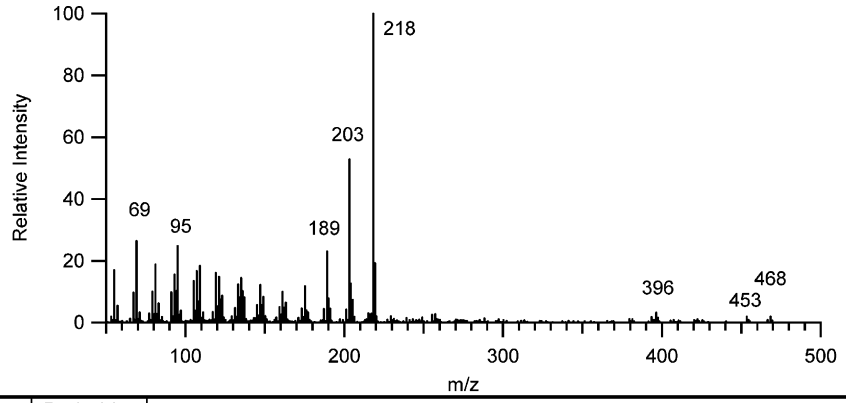

| ? | Probably 316 | Peak 2 from Daemonorops micracantha |
|---|---|---|



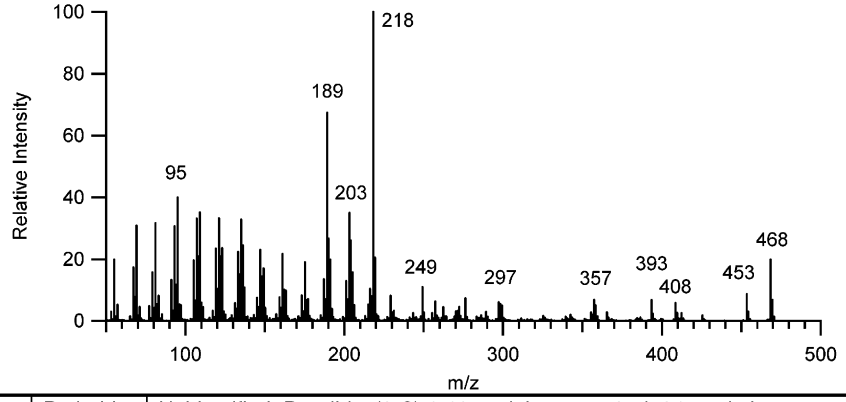
## Appendix B

Mass spectra of unknown triterpenoid substances on the amber game box, Dresden.

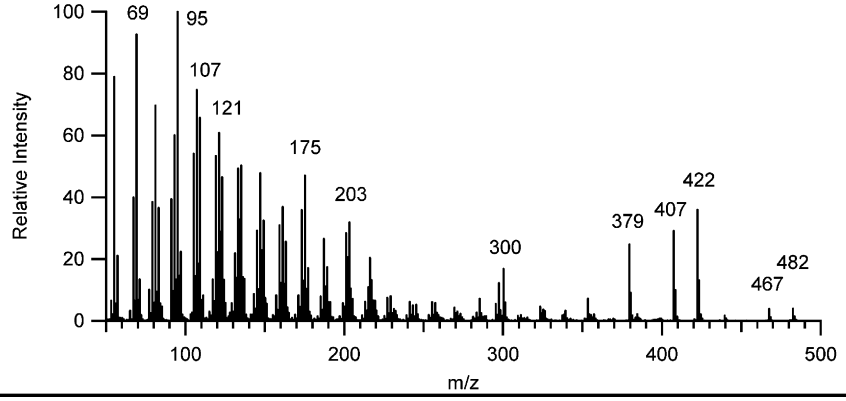
| Formula | MW | Trivial name |
|---|---|---|
| ? | Probably 468 | Unidentified. Possibly: β-amyrin acetate, boswellic acid derivative or commic acid derivative |




| ? | Probably 468 | Unidentified. Possibly: β-amyrin acetate, boswellic acid-derivative or comic acid derivative |
|---|---|---|




| Possibly $C_{33}H_{54}O_2$ | Probably 482 | Unidentified. Possibly: (3-ß)-9,19-cyclolanostan-3-ol, 24-methylene acetate |
|---|---|---|

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