Study of thermal behavior and molecular composition of mixtures of resinous materials and beeswax found as adhesives in archaeological finds

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A R T I C L E   I N F O

A B S T R A C T

Beeswax and resinous materials have been used and combined since ancient times to obtain adhesives. In this work, we studied mixtures of these two materials under heating to investigate the effect of their interactions on the properties of the resulting adhesive. The results were then compared with those of archaeological samples, to obtain new insights into ancient technological knowledge. This study was performed by combining two different chemical-analytical techniques: evolved gas analysis coupled with mass spectrometry and flow injection analysis-high resolution mass spectrometry. Evolved gas analysis was used to investigate the thermal behavior of the mixtures and obtain information on production techniques and ageing processes. The data were processed by isoconversional method to estimate the activation energies associated with the thermal degradation of the adhesives. The results suggested that archaeological mixtures were subjected to a thermal pre-treatment before their use as adhesives and that heating led to a material with new chemical features, due to the formation of hybrid species between resin diterpenes and the beeswax compounds. The formation of these species was confirmed by high resolution mass spectrometry.

1. Introduction

Beeswax and pine resin are among the most ubiquitous organic materials recovered as adhesives from archaeological finds [1]. In particular, pine resin can be found either in its natural form or as tar and pitch, products obtained by subjecting resinous wood to pyrolysis-like processes [2–4]. Adhesives found in archaeological objects are often constituted of mixtures of resinous substances and other materials, such as beeswax or animal fats, which were added to improve the adhesive properties of the formulation by modifying the physical-chemical properties of the resinous substances [1,5–7].

Due to their complexity, the study of the composition of these materials requires the use of instrumental techniques capable of molecular-level characterization, and mass spectrometry-based techniques are particularly suitable for this purpose [3,6]. In addition, the use of such techniques allows us to gain insights into the chemical transformations due to natural aging and anthropogenic treatments [1,3,4,6,8].

In this view, the detection of key molecular species generated by the chemical interactions between the mixture components is fundamental [16–20]. In a previous study, we showed that flow injection analysis (FIA) coupled with high-resolution mass spectrometry through an ESI

source (ESI-Q-ToF) could be used to detect the presence of hybrid species resulting from reactions between diterpenoids and fatty acids/hydroxy fatty acids from pine resin and beeswax, respectively [17]. The formation of esters between the constituents of pine resin and beeswax was attributed to the mixing and heating processes typically used to produce adhesive, suggesting not only an intentional addition but also an advanced technological knowledge on the properties of materials. Direct analysis by FIA-MS allowed us to overcome the limitations of chromatographic techniques, such as the need for a hydrolysis or a thermal decomposition step which could lead to a possible loss of information on the original composition of the organic residues and on the structure of high molecular weight components. Correlating the molecular composition of adhesives with their physical-chemical properties is also fundamental to understand the reasons for their success in ancient history. In particular, the study of the thermal behavior is crucial to understand the treatments underwent by the original materials and their preservation state. Evolved gas analysis coupled to mass spectrometry (EGA-MS) is a powerful technique to study the thermal behavior of complex organic samples and to determine the nature and amount of volatile products formed during the thermal degradation of materials or the occurrence of cross-linking phenomena [9,21].

Recently, EGA-MS has been used to estimate kinetic parameters of the thermal degradation of organic materials through isoconversional methods [22–24]. Isoconversional methods are a group of macroscopic modelling methods which provide kinetic data about complex systems [22,25–27]. Model-free isoconversional methods are a sub-category of such methods, that estimate the apparent activation energy of a reaction without any assumption on its mechanism. Estimating the activation energy of a pyrolytic process can provide useful information on the energetics of the process.

In this work, we combined EGA-MS and FIA-HRMS to study both reference and archaeological mixtures of resinous substance and beeswax, as well as mixtures of their characteristic single components (abietic acid and hexadecyl palmitate). EGA-MS was used to study the thermal behavior and the thermo-chemistry of the mixtures. The obtained data were processed by isoconversional method, to understand the variation of the thermal behavior of the mixtures before and after heating, while FIA-HRMS was used to detect the formation of hybrid resin-beeswax molecular species upon heating of the reference mixtures.

2. Experimental

2.1. Chemicals

Abietic acid (75%, Sigma-Aldrich) and hexadecyl palmitate (95% Sigma-Aldrich) were used to prepare reference mixtures. Acetone (HPLC grade, Sigma-Aldrich) was used for homogenization of the mixtures. Chloroform, hexane (HPLC grade, Sigma-Aldrich) and isopropanol (HPLC grade, Fluka) were used as solvents for FIA-HRMS analyses.

2.2. Samples

Beeswax and resin from *Pinus pinaster* were purchased locally, while archaeological pitch (P) was taken from the bottom of an amphora found in the archaeological site of Medinet Madi Fayum (Egypt), dating back to 2nd-3rd century BC [4]. Binary reference mixtures were obtained by mixing abietic acid (AA), hexadecyl palmitate (HP), beeswax (B) pitch (P) and pine resin (R) (1:1 mass ratio). Homogeneous mixtures were obtained by suspending the components in 1 mL acetone and then sonicating the suspensions (Bandelin Sonorex Digitec, 15 min at room temperature). Additional reference samples were also obtained by heating the mixtures at 200 and 300 °C in oven for 1 h and 2 h. Table 1 summarizes the mixtures produced and the heating conditions. These heating conditions were determined in a previous step of the analysis. For the temperature, the experiments were performed starting from melting point of beeswax (62–64 °C) and pine resin (70–135 °C) to the optimal temperatures, while for the time it was observed that results obtained were not significantly different by heating the samples for one hour or two hours.

Six archaeological samples collected from the archaeological site of Antinoe (Egypt, 4th-5th century AD) were used in this study. Their composition has already been determined in a previous work [6]. Table 2 lists all archaeological samples and their composition.

2.3. Evolved gas analysis-mass spectrometry (EGA-MS)

2.3.1. EGA-MS analysis

All experiments were performed with an EGA/PY-3030D micro-furnace pyrolyzer (Frontier Laboratories, Japan) coupled to a 6890 gas chromatograph equipped with a split/splitless injector and a 5973 mass spectrometric detector (Agilent Technologies, USA). During each experiment, the furnace temperature was raised from 50 °C to 800 °C at six different heating rates (β = 15, 20, 25, 30, 35, and 40 °C/min). The interface between the furnace and the GC injector was kept 100 °C above the furnace temperature, to a maximum of 320 °C. The GC injector was operated in split mode with a 30:1 ratio at 300 °C. The pyrolyzer and mass spectrometer were connected by an Ultra-ALLOY deactivated and uncoated stainless-steel capillary tube (UADTM-2.5 N, 2.5 m x 0.15 mm, Frontier Laboratories, Japan), which was kept at 300 °C. Helium (1.2 mL/min) was used as carrier gas. The mass spectrometer was operated in EI positive mode (70 eV, m/z range 50–300). The ion source and quadrupole analyzer were kept at 230 °C and 150 °C, respectively.

2.3.2. Isoconversional method

Conversion profiles were calculated from the EGA-MS profiles using Eq. (1), where S is the total ion current of the mass spectrometer as a function of the temperature T, T_0 the initial temperature, and A_{TOT} is the total area of the thermogram. The Kissinger-Akahira-Sunose isoconversional method was used to calculate the apparent activation energy for the thermal degradation of the samples. The equation for this method is (2), where α is the conversion, β is the heating rate, E_a the apparent activation energy, R the gas constant and r(α) is a function of the conversion. For a fixed value of α, the equation gives a linear trend of the left side as a function of 1/T. The slope of these functions can be directly related to the apparent activation energy [22,24–26].

$$\alpha = \frac{1}{A_{TOT}} \int_{T_0}^{T} S(\tau)d\tau \qquad (1)$$

$$\ln\left(\frac{\beta}{T^2}\right) = -\frac{E_a}{RT} + r(\alpha) \qquad (2)$$

2.4. Flow-injection analysis-high resolution mass spectrometry (FIA-HRMS)

Approximately 0.1 mg of a reference mixture and archaeological sample were subjected to ultrasound-assisted extraction at room temperature using 1 mL and 500 μL of a 3:2 v/v chloroform:hexane mixture for 15 and 20 min, respectively. In both cases, 20 μL of the obtained mixture were diluted in isopropanol (1:4000). The initial extraction step allowed us to increase the amount of extracted material and avoid secondary transesterification of beeswax esters, which could cause an alteration in the profile of the material [28,29]. Sonication was used to increase efficiency and reduce extraction time [30,31].

The analysis was carried out using a 1200 Infinity HPLC coupled to a Jet Stream ESI interface with a 6530 Infinity Q-ToF quadrupole-time of

Table 1
List of reference mixtures produced and their heating conditions. AA = abietic acid; HP = hexadecyl palmitate; B = beeswax; R = resin; P = pitch.

Mixture	Heating conditions
AA+HP	200 °C, 2 h
	300 °C, 1 h
AA+B	200 °C, 2 h
	300 °C, 1 h
R+HP	200 °C, 2 h
	300 °C, 1 h
R+B	untreated
	200 °C, 2 h
	300 °C, 1 h
P + B	untreated

Table 2
List of the archaeological samples and their composition. B = beeswax; P = pitch.

Sample	Composition
A3	P + B
C5	P + B
C6a	P + B
D1a	P + B
D2a	B
D2bs	P + B

flight tandem mass spectrometer (Agilent Technologies, US). The eluents were methanol:water (85:15) and isopropanol; the flow rate was 0.2 mL/min and the injection volume was 1 μL. The mass spectrometer was calibrated using the HP0321 tuning mix (Agilent Technologies, USA). The ESI operating conditions were: drying gas (N_2, purity > 98%): 350 °C and 10 L/min; capillary voltage 4.5 kV; nebulizer gas 35 psig; sheath gas (N_2, purity > 98%): 375 °C and 11 L/min. High resolution MS spectra were acquired in positive mode in the range 100–3200 m/z. The acquisition time for full scan analysis was 1.5 min.

3. Results and discussion

3.1. EGA-MS and isoconversional method

EGA-MS was used to study the thermal behavior and the thermochemistry of the mixtures starting from the reference samples. Fig. 1 shows the thermograms obtained for R+B$_{untreated}$, R+B$_{300}$ and P + B$_{untreated}$ at a heating rate of 40 °C/min, while the relative average mass spectra are reported in Fig. 2. Several experiments were carried out varying the heating rate and Table 3 lists the temperatures of the signal maxima for each heating rate for the various reference mixtures.

The signal peak in the mixture of pitch and beeswax was at higher temperatures than in the samples that contained beeswax and pine resin, even after heating. In particular, the signal peak for samples with pine resin was below 300 °C, while it was higher than 300 °C for sample P + B. 300 °C is the temperature to discriminate between thermal desorption and pyrolysis; therefore, it is possible to assert that the pyrolysis of a polymerized/cross-linked fraction took place in sample P + B$_{untreated}$, while the thermal desorption of free molecular species was the main phenomenon in samples R+B$_{untreated}$ and R+B$_{300}$. In any case, R+B$_{untreated}$ and R+B$_{300}$ show different behaviors under heating. In fact, the temperature of signal peak generally decreased going from R+B$_{untreated}$ to R+B$_{300}$(Table 3) or remained almost the same at the heating rate of 40 °C/min. These results may be attributed to the fact that the species desorbed from the heated sample were more defunctionalized and aromatized than those from the untreated ones.

As support, Fig. 2 shows the average mass spectra of samples R+B$_{untreated}$ and R+B$_{300}$. The mass spectrum of sample R+B$_{untreated}$ (Fig. 2a) was mainly characterized by the peaks at m/z 241, 259, 287 and 302 ascribable to abietic acid, while the mass spectrum of R+B$_{300}$ (Fig. 2b) showed peaks at m/z 197, 239, 285 and 300, and 298 and 237 ascribable to abieta-8,11,13-trienoic acid and abieta-6,8,11,13-
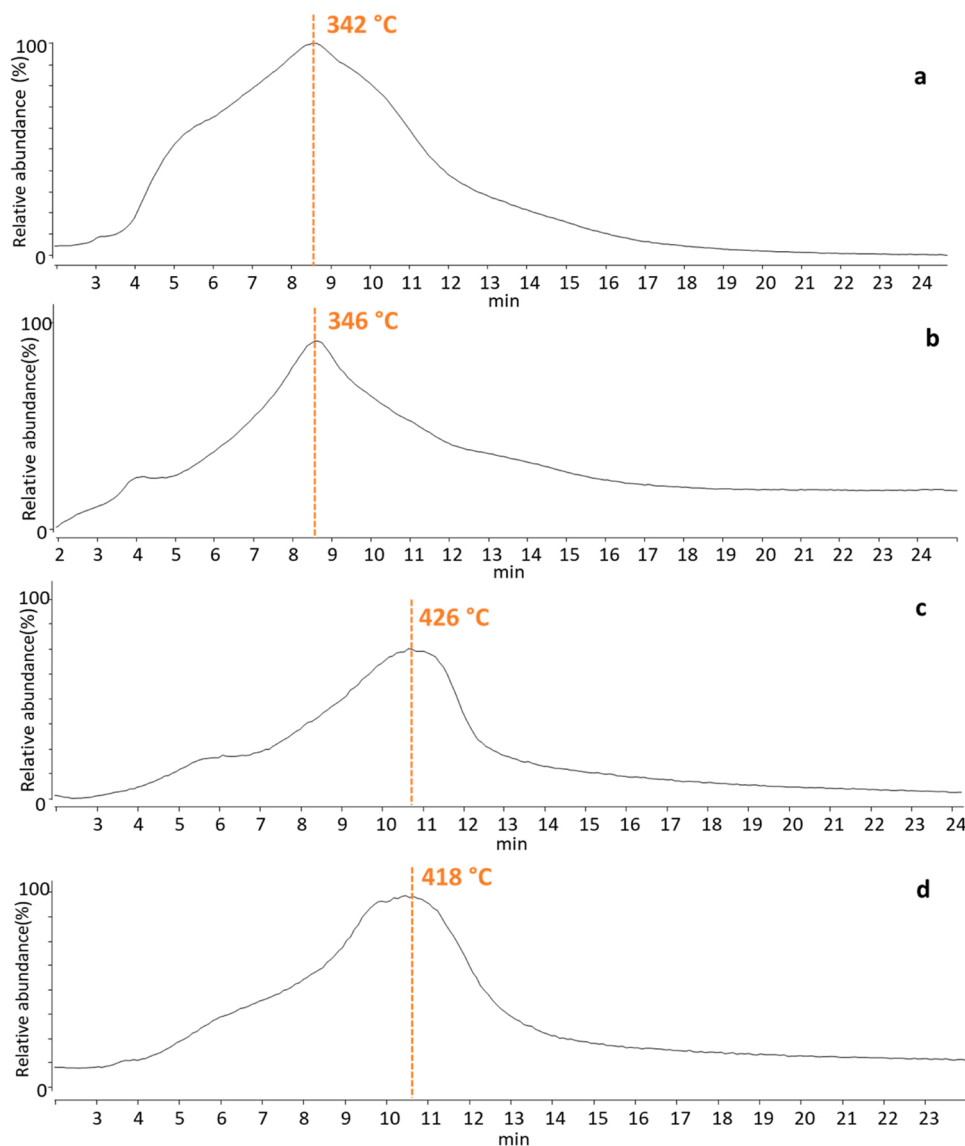

Fig. 1. Thermograms obtained at the heating rate of 40 °C/min for references mixtures a) R+B$_{untreated}$, b) R+B$_{300}$ and c) P + B$_{untreated}$ and d) archaeological sample C6a. The temperature of signal maximum is shown for each thermogram.
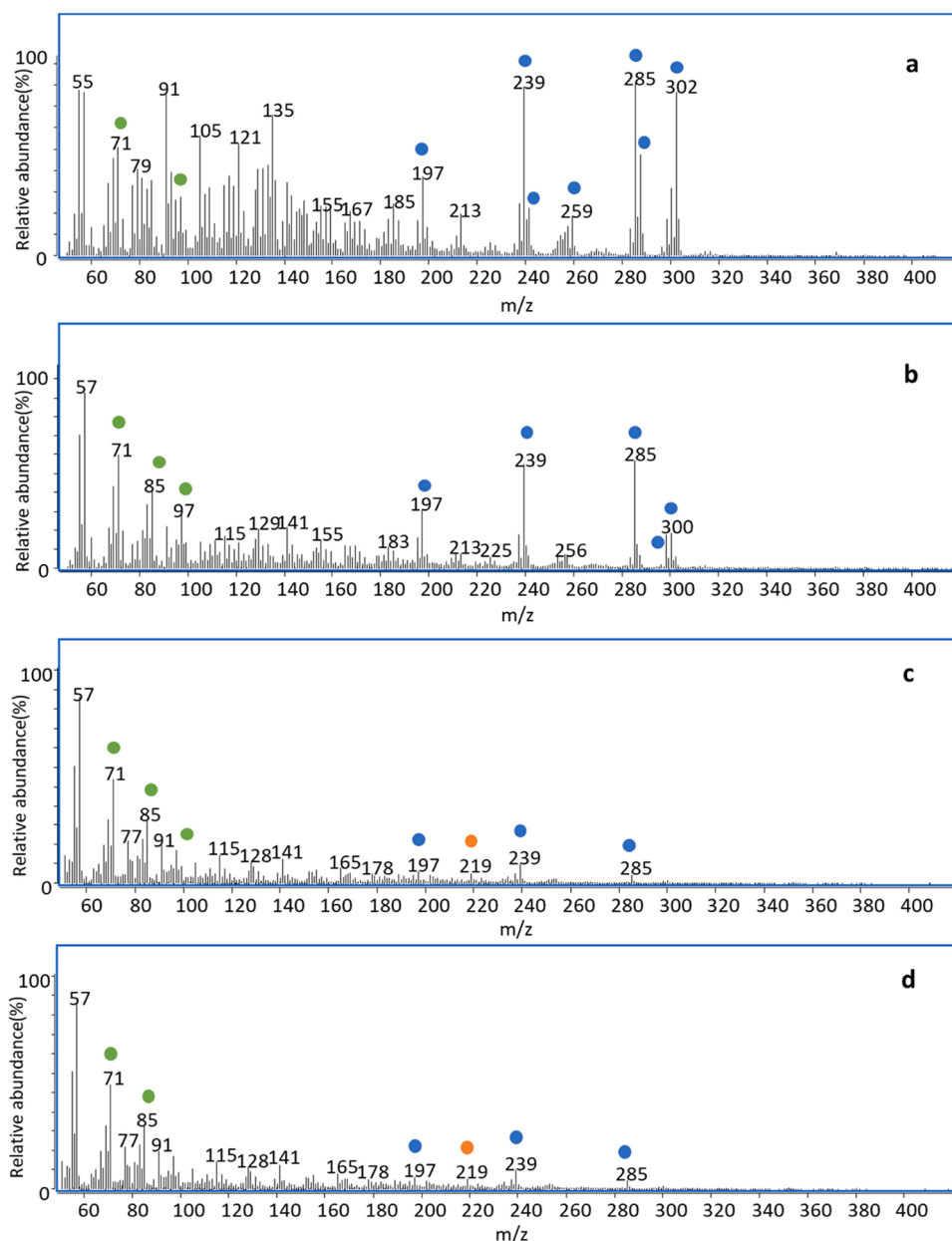
Fig. 2. Average mass spectra of the thermograms reported in Fig. 1: a) R+B$_{untreated}$, b) R+B$_{300}$, c) P + B$_{untreated}$ and d) C6a. In each mass spectrum, the green dots (•) indicate the *m/z* signals ascribable to desorption/pyrolysis products of beeswax, the blue dots (•) indicate signals of pine resin, and the orange dots (•) indicate signals of pine pitch.

Table 3
Peak temperatures for each heating rate for the reference mixtures.

Heating rate	R+B$_{untreated}$	R+B$_{300}$	P + B$_{untreated}$
15 °C/min	201	173	–
20 °C/min	224	190	–
25 °C/min	257	211	392
30 °C/min	328	245	388
35 °C/min	352	326	402
40 °C/min	342	346	426

tetraenoic acid. These compounds will be addressed as dehydroabietic acid and didehydroabietic acid, respectively, in the remainder of the paper [4]. Their presence, combined with the absence of signals ascribable to abietic acid, confirms that the formation of unsaturated diterpenoid compounds was favored at the expense of abietic acid when the mixture was heated during preparation. The signals at *m/z* values 71,

85, 99 and 69, 83, 97, 111 in each mass spectrum can be ascribed to the alkanes and alkenes, respectively, deriving from the hydrocarbon chains and fatty acids and esters of beeswax [5]. The average mass spectrum of the sample P + B$_{untreated}$ showed high intensities of the signals of unsaturated diterpenoid compounds, but also showed a significant intensity of *m/z* 219, that can be ascribed to retene, a molecular maker obtained from abietic acid and its derivatives during the heating of resin to produce pitch.

By applying the isoconversional method to the data obtained from EGA-MS we obtained the following values of apparent activation energy values: $1.68 \pm 0.3 \cdot 10^4$ J mol^{-1} and $2.26 \pm 0.4 \cdot 10^4$ J mol^{-1} for samples R+B$_{untreated}$ and R+B$_{300}$, respectively, and $3.89 \pm 0.7 \cdot 10^4$ J mol^{-1} for P + B$_{untreated}$. The apparent activation energies of heated references were higher than that of untreated samples, highlighting that the thermal pre-treatment and the ageing led to the removal of the more volatile components, promoting the formation of higher molecular weight

species through cross-linking reactions. As a further confirmation, the final part of the thermogram of R+B$_{300}$ shows a higher signal intensity than the thermogram of R+B$_{untreated}$, while the opposite is true for the signals at lower temperatures. Fig. 1 and Fig. 2 show also the thermograms and the resulting mass spectrum obtained for a representative archaeological mixture of pitch and beeswax, sample C6a (Fig. 1d). EGA-MS results for the other archaeological samples are available in the Supplementary Material.

The thermograms obtained for the archaeological samples are consistent with the thermal behavior highlighted for the reference mixture P + B$_{untreated}$ rather than the two mixtures containing pine resin.

The average mass spectra associated with the thermograms are dominated by signals ascribable to beeswax components and by m/z 316 and 330, ascribable to oxidized terpenes such as 7-hydroxyabieta-8,11,13-trienoic acid (7-hydroxydehydroabietic acid) and 15-hydroxy-7-oxoabieta-8,11,13-trienoic acid (15-hydroxy-7-oxodehydroabietic acid), together with dehydroabietic acid and 7-oxodehydroabietic acid. The m/z values 219 and 234, ascribable to retene, were also found in these samples.

The thermograms of the archaeological samples showed a peak above 300 °C, similar to that observed for sample P + B$_{untreated}$, and, also in this case, in the final part of thermograms the ion current remained high. In addition, the activation energy values increased further, to approximately $6.00 \cdot 10^4$ J mol^{-1}. This highlights that, in a similar way to heating, aging promoted the increment of cross-linking reactions and the formation of high molecular weight species in archaeological samples.

Further information on the generation of a macromolecular network can be obtained by comparing the extracted ion thermograms of different samples obtained from distinct m/z values, characteristic of dehydroabietic acid. Fig. 3 compares the extracted ion thermograms for m/z 197 (a), 239 (b) and 285 (c) of reference samples R+B$_{untreated}$,

R+B$_{300}$ and P + B$_{untreated}$, and archaeological sample C6a. The temperature of signal maximum for these ions was at significantly higher values for the two samples containing archaeological pitch. This indicates that the presence of pitch is the main responsible for the higher thermal stability. Interestingly, sample R+B$_{300}$ did not show any significant shift of the temperature of signal maximum compared to R+B$_{untreated}$, indicating that the formation of the cross-linked network is mostly formed during the ageing of pitch, rather than during its preparation.

3.2. FIA-HRMS

Flow-injection experiments of heated reference mixtures provided complex mass spectra, as shown in Fig. 4(a) and (b). These mass spectra showed clusters of signals that could be ascribed to resinous and beeswax components, both as free molecules and as oligomers [17]. In comparison to sample R+B$_{200}$, sample R+B$_{300}$ showed a higher relative intensity of the signals corresponding to free fatty acids of beeswax and monomeric diterpenoids of resin compared to the intensities of the clusters of oligomers. This indicates that heating of the mixtures favors the cleavage of ester bonds of higher-molecular weight oligomers to give lower-molecular weight ones. Moreover, the clusters corresponding to beeswax oligomers in sample R+B$_{300}$ showed a greater number of m/z signals with high relative intensities than the corresponding clusters in sample R+B$_{200}$. This indicates that the oligomers are not only degraded to smaller aggregates, but also chemically modified. The most likely hypothesis in this case is a partial oxidation of the oligomers taking place during heating. This is highlighted in Fig. 5, showing the portion of the mass spectra of samples R+B$_{200}$ and R+B$_{300}$ characteristic of beeswax monoesters and resin dimers. As can be observed, the same species responsible for some of the signals in sample R+B$_{200}$ can be found in sample R+B$_{300}$ at different m/z values, due to either the addition of oxygen or the loss of H$_2$ after the more intense heating.
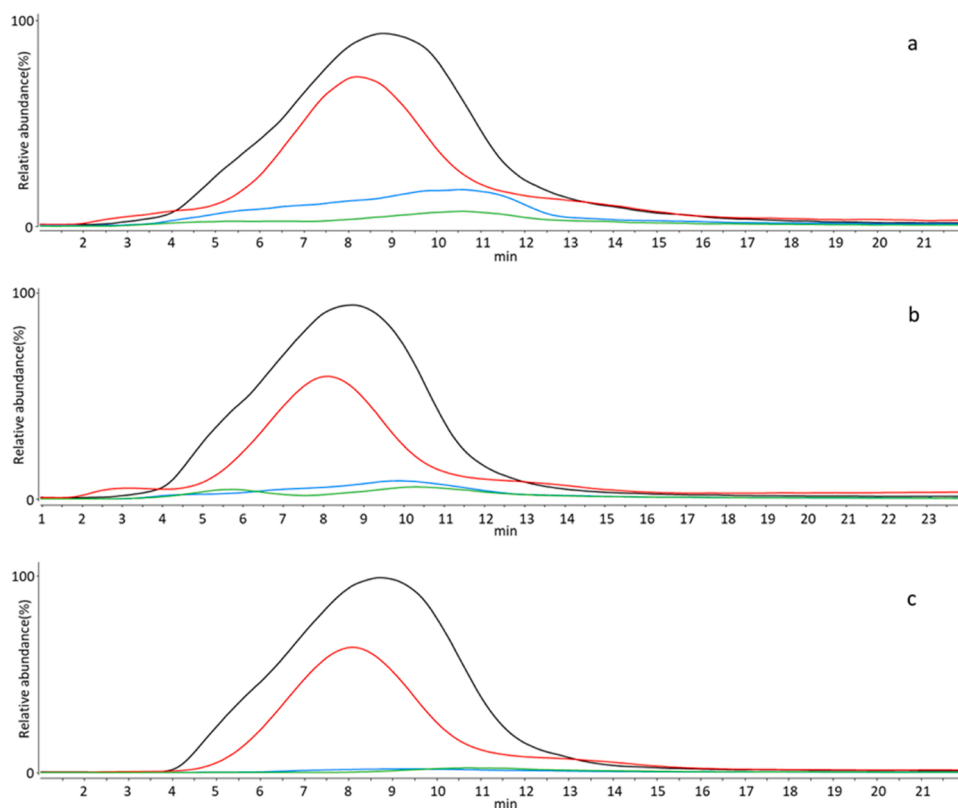

Fig. 3. Extracted ion thermograms of a) m/z 197, b) m/z 239 and c) m/z 285 respectively. Black profiles (●) correspond to R+B$_{untreated}$, red profiles (fx5) to R+B$_{300}$, blue profiles (fx4) to P + B$_{untreated}$, and green profiles (fx1) to archaeological sample C6a.
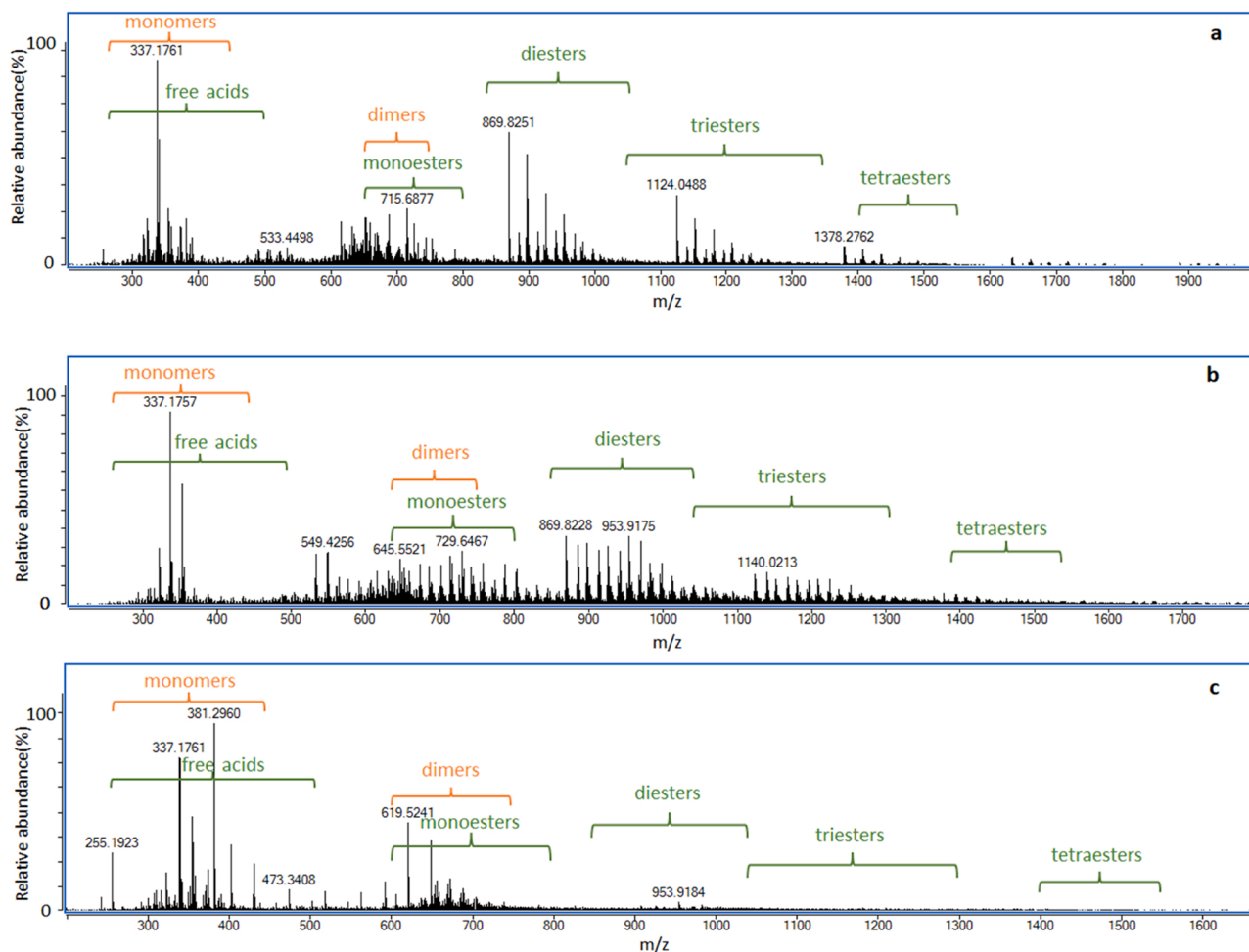
Fig. 4. FIA-HRMS average mass spectra of sample a) R+B$_{200}$, b) R+B$_{300}$ and c) sample D2bs. In each spectrum, clusters highlighted in green indicate m/z signals ascribable to ionization and fragmentation of beeswax components, while clusters highlighted in orange indicate those of pine resin.
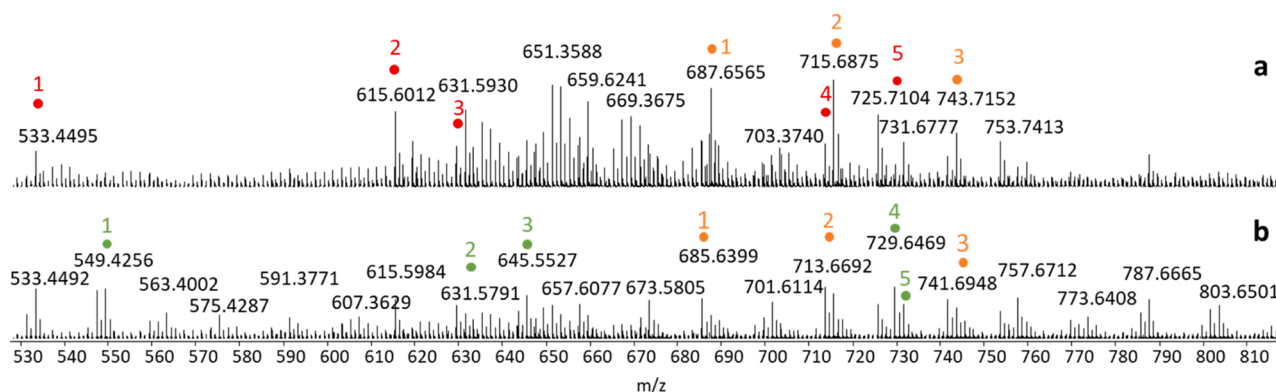

Fig. 5. Mass spectra of a) R+B$_{200}$ and b) R+B$_{300}$. Red dots (•) indicate the precursor, while green dots (•) and orange dots (•) indicate the specie after the addition of oxygen and the loss of H$_2$, respectively.

Finally, sample R+B$_{300}$ also showed a small number of m/z signals that could be ascribed to hybrid compounds, generated by the formation of ester bonds between beeswax and resin components. These compounds were also detected in the mass spectra of the mixtures of reference abietic acid and beeswax heated at 300 °C. Proposed structures for these hybrid compounds are shown in Fig. 6(a) and (b). Confirmation of the proposed structures was based on their MS/MS fragmentation patterns. Fragmentation examples are presented in Fig. 7, which shows the tandem mass spectra of the hybrid species identified in sample AA+B$_{300}$.

Samples heated at lower temperatures did not show these signals, indicating that the threshold temperature required for their formation is between 200 °C and 300 °C.

Signals ascribable to hybrid species were also detected in the mass spectra of archaeological samples, as shown in Fig. 6(c). A complete list of all hybrid compounds is presented in Table 4. The archaeological sample with the highest number of hybrid compounds was D2bs, while no hybrid compounds were detected in samples C5, D1a and D2a. Archaeological samples were only partially solubilized in the injection
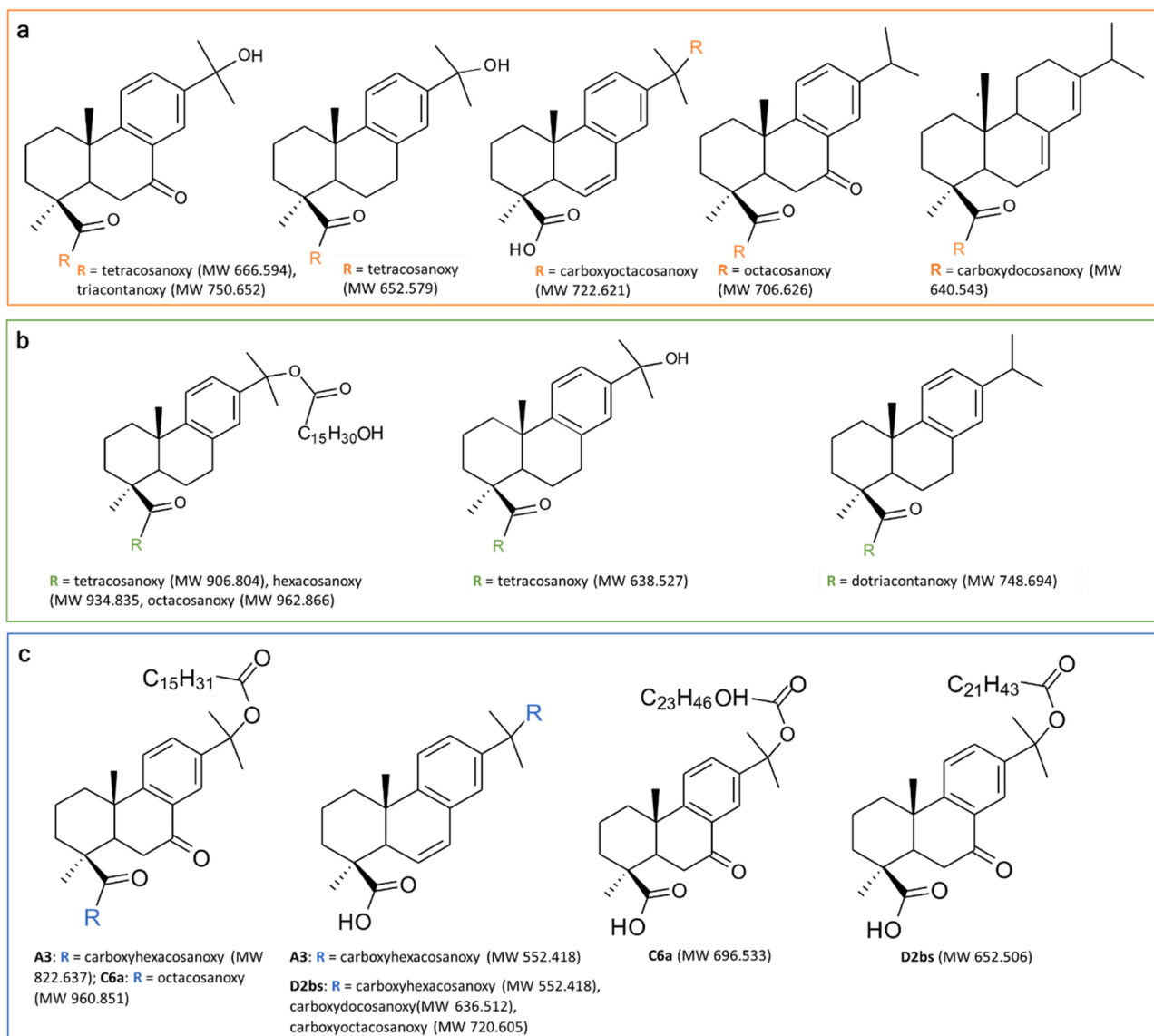
Fig. 6. Structures of resin-wax esters detected in a) AA+B$_{300}$, b) R+B$_{300}$ and c) archaeological samples, correlated to Table 4. Molecular weights are also shown for each compound.

solvent used for flow-injection analyses. This is likely due to the formation of a polymeric network during the ageing of these samples, as already hypothesized from the EGA-MS results. This is consistent with the higher apparent activation energies obtained for the archaeological samples compared to the reference mixtures. The low solubility of archaeological samples is the most likely explanation for the lower signals obtained in their mass spectra (Fig. 4(c)), especially for the beeswax oligoesters, and for the absence of signals ascribable to hybrid compounds.

It is interesting to notice that the ester bonds in the hybrid compounds of the reference mixtures mostly involve the carboxy group of abietane acids and long chain alcohols of beeswax. As free alcohols are almost absent in fresh beeswax [1], we can conclude that the most likely reaction mechanism leading to the formation of hybrid compounds is trans-esterification of the beeswax esters with abietane acids. It is also worth noting that the hybrid compounds obtained in the reference mixtures involve both oxidized and non-oxidized abietic acid. This indicates that oxidation of abietic acid and formation of hybrid compounds have similar reaction rates under the heating conditions adopted in this study.

Contrary to the reference samples, the ester bonds in archaeological samples mostly involve free fatty acids from beeswax and the hydroxy group at position 15 of the abietane acids, which is a result of the oxidation of resin compounds. This indicates that, for the archaeological samples, oxidation of abietane acids took place before trans-esterification reactions. The reason for this is most likely that pitch, rather than fresh resin, was used to prepare the archaeological mixtures, as pitch is richer in oxidized abietane acid.

The presence of ester bonds involving the hydroxy group at position 15 of abietane acids should not hinder the formation of other ester bonds involving the carboxy group. However, such ester bonds were not detected in the hybrid compounds of archaeological samples. This leads us to conclude that trans-esterification reactions induced by heating of the mixtures at 300 °C were not favored during the preparation of the archaeological mixtures, meaning that the mixtures were heated at lower temperatures.

With this conclusion, a question remains on how the ester bonds could have been formed in the archaeological adhesives. The most likely explanation is that the hybrid species are not a result of heating, but rather of ageing. During ageing, the esters of beeswax undergo hyrolysis to give free carboxylic acids, which can then generate the hybrid species with oxidized abietane acids without the need of high temperatures.
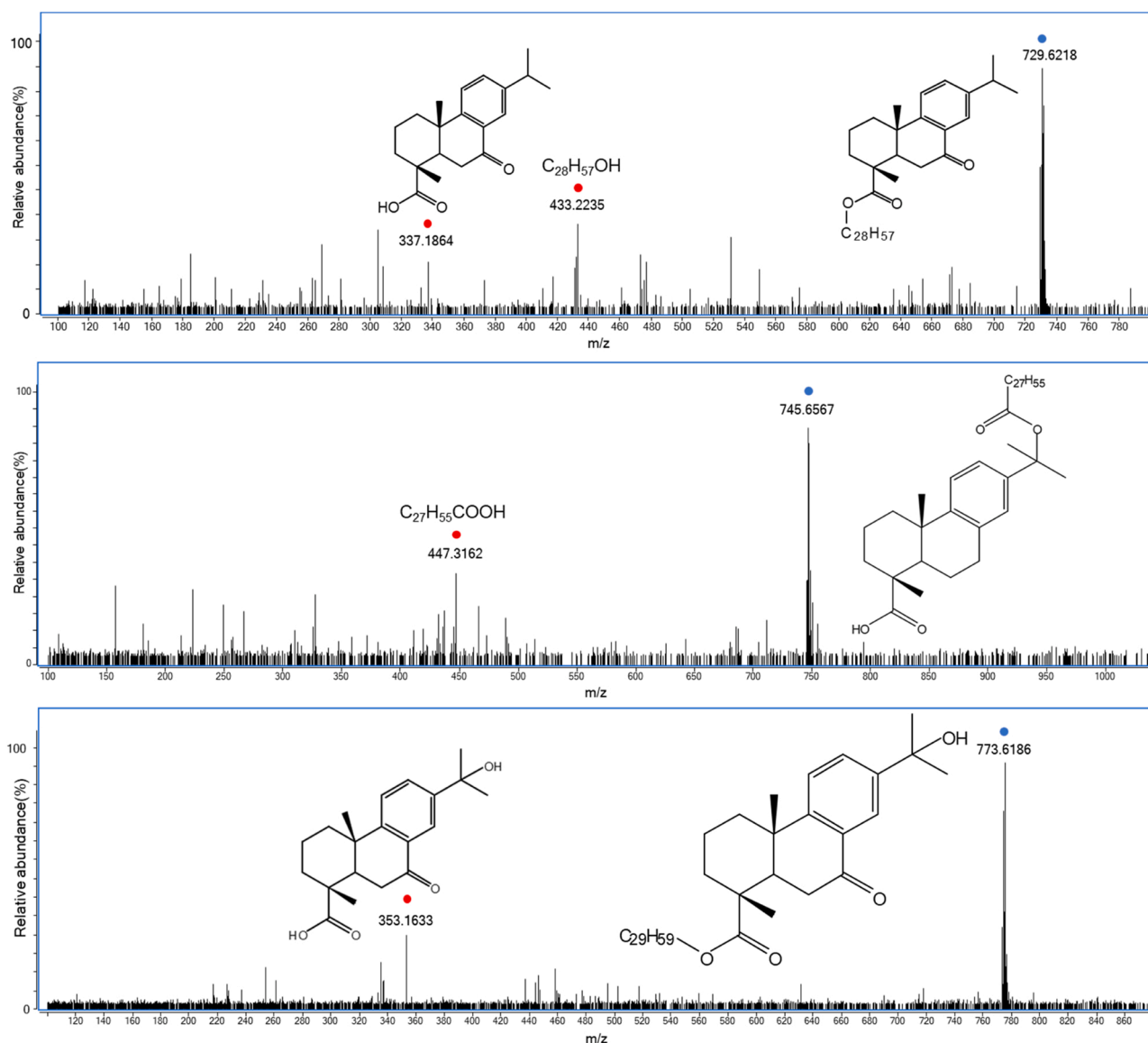
Fig. 7. Tandem mass spectra of hybrid esters found in reference sample AA+B$_{300}$. Blue dots (•) represent the precursor ion, while red dots (•) correspond to the identified fragments.

4. Conclusions

The formation of new hybrid species between diterpenoids of the resinous and beeswax components has been confirmed both by EGA-MS and FIA-HRMS. Structures of these hybrid components hypothesized from the FIA-HRMS spectra strongly suggest that trans-esterification reactions are the main mechanisms responsible for their formation. In EGA-MS analyses, the shift of the signal peak temperature from reference samples containing pine resin to mixture containing pitch and archaeological samples suggested the formation of species with high molecular weights and reticulated fractions. This was confirmed by the calculated values of apparent activation energy. The formation of high molecular weight species, including resin-beeswax hybrid esters, was also highlighted by data obtained from FIA-HRMS. Flow injection analyses suggested that the formation of high molecular weight species occurred after heating the reference mixture at 300 °C. Hybrid species were also found in archaeological samples, but with different structures, suggesting that their formation is more likely due to hydrolysis of beeswax esters during ageing, and that the archaeological adhesives were heated at lower temperatures than the ones used for the references.

CRediT authorship contribution statement

Irene Bertelli: Conceptualization, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Marco Mattonai:** Conceptualization, Methodology, Software, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Jacopo La Nasa:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Erika Ribechini:** Conceptualization, Resources, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 4

Detected and predicted *m/z* signals in FIA-HRMS spectra and corresponding structures.

Sample	*m/z* [M+Na]⁺ Predicted	*m/z* [M+Na]⁺ Detected	Compound
AA+B₃₀₀	689.548	689.551	15-Hydroxy-7-oxodehydroabietic acid + tetracosanol
	729.616	729.622	7-Oxodehydroabietic acid + octacosanol
	773.642	773.645	15-Hydroxy-7-oxodehydroabietic acid + triacontanol
	663.533	663.532	Abietic acid + hydroxydocosanoic acid
	675.569	675.567	15-Hydroxydehydroabietic acid + tetracosanol
	745.611	745.657	15-Hydroxydehydroabietic acid + octacosanol
R+B₃₀₀	661.517	661.513	15-Hydroxydehydroabietic acid + tetracosanol
	771.684	771.706	Didehydroabietic acid + dotriacontanol
	929.794	929.793	Hydroxypalmitic acid + 15-Hydroxydehydroabietic acid + tetracosanol
	957.825	957.825	Hydroxypalmitic acid + 15-Hydroxydehydroabietic acid + hexacosanol
	985.856	985.863	Hydroxypalmitic acid + 15-Hydroxydehydroabietic acid + octacosanol
A3	575.408	575.404	15-Hydroxydidehydroabietic acid + palmitic acid
	845.627	845.615	15-Hydroxy-7-oxodehydroabietic acid + palmitic acid + hydroxypalmitic acid
C6a	719.523	719.520	15-Hydroxy-7-oxodehydroabietic acid + hydroxytetracosanoic acid
	983.841	983.843	15-Hydroxy-7-oxodehydroabietic acid + palmitic acid + octacosanol
D2bs	575.408	575.406	15-Hydroxydidehydroabietic acid + palmitic acid
	659.502	659.500	15-Hydroxydidehydroabietic acid + docosanoic acid
	675.496	675.497	15-Hydroxy-7-oxodehydroabietic acid + docosanoic acid
	743.595	743.592	15-Hydroxydidehydroabietic acid + octacosanoic acid

Data Availability

Data will be made available on request.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2023.105936.

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