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Infrared spectroscopic study of the formation of fossil resin analogs with temperature using *trans-c*ommunic acid as precursor

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Abstract

For million years resin exudates have undergone chemical alterations by heat, pressure, radiation, water, oxygen, microorganisms, and have suffered processes of sedimentation and diagenesis. These agents have affected the organic functional groups present in the terpenes of the resins, giving rise to what we nowadays know as fossil resins. In this work, we try to get further insight in the chemical formation of fossil resins. As the simulation of the natural process is quite complex, we have focused on the temperature induced reactivity of the *trans*-communic acid, the main component of the *Class* I resins. Using this terpene derivate as a very basic model of a resin exudate, we have monitored their thermal changes by infrared spectroscopy, differential scanning calorimetry and thermogravimetric analysis within the range of 25 to 340 ºC. The temperature-induced transformation, both in presence and absence of inert atmosphere, is discussed on the basis of the reactivity of the conjugated double-bond, the exocyclic bond and the carboxylic acid group present in the *trans*-communic acid. The results obtained in these series of experiments agree with the maturation scheme accepted in the literature for natural resins, i.e. an initial cross-linked polymerization and a subsequent maturation reaction. From combined DSC/TGA and infrared spectroscopy results, we conclude that chemical changes produced in the *trans*-communic acid in the range 130-175 ºC may mimic the initial polymerization-like process in the natural resins, whereas those produced between 180 to 340 ºC seem to correspond to the maturation pathways described in the literature for fossil resins *Class Ib*. Spectral assignment of the most relevant infrared-active modes of the *trans*-communic acid at 25 ºC is also provided with the aid of Density Functional Theory calculations.

Keywords: Infrared Spectroscopy; Communic Acid; Fossil Resins; Amber.

1.   Introduction

Amber and other fossil resins are wanted not only by jewelry collectors but also by scientists, since these substances allow us to record Earth's History. Fossil resins are not ores but fossilized organic matter from ancient trees naturally formed by the cross-linked polymerization of organic compounds. Fossil resins are mostly derived from natural terpenes-based polymers and therefore have an organic origin [1,2]. They are

found in Cretaceous and Tertiary sedimentary rocks, especially in clays, shales and sandstones associated with lignite. The special case of Baltic amber also appears on beaches bathed by the sea because of their low density, so they float in salt water.

Fossil resins have been discussed in the literature according to their specific geographic origin or their chemical and botanical affinities [3]. However, due to the wide variety of fossil resins, it is not easy to establish a unified classification. Currently, the most complete and widely accepted classification is due to Anderson *et al.* [4], which is based on structural and compositional characteristics. This classification groups the fossil resins into five *Classes* (*I, II, II, IV* and *V*), depending on their chemical-structural features. *Class I* is the most important for the purposes of this work and Baltic amber is the most characteristic example. Class I includes natural terpene-based substances composed primarily of cross-linked polymers of high-molecular weight. More specifically, *Class I* compounds derive mainly from resins based on co-polymers of labdatriene carboxylic acids (*e. g.* monomers of 8(17), 12(13)14-labdatriene-18-oic acid), and their reduced forms (Fig. 1). The wide diversity of amber belonging to *Class I* has resulted in the definition of four subclasses:

- *Class Ia*: based primarily on polymers of communic acid, partially co-polymerized with biformene and communol, probably as a cross linking agent characteristic, having the regular [1*S*, 4a*R*, 5*S*, 8a*R*] configuration (Fig. 2). A significant incorporation of succinic acid is usually found.
- *Class Ib:* similar to *Class Ia* but succinic acid is absent [5].
- *Class Ic:* based primarily on polymers of ozic acid and/or zanzibaric acid, having the *enantio* [1*S*, 4a*S*, 5*R*, 8a*S*] configuration [6].
- *Class Id:* derived from/based on polymers and co-polymers of labdanoid diterpenes having the *enantio* [1*S*, 4a*S*, 5*R*, 8a*S*] configuration, including but not limited to ozic acid, ozol and *enantio* biformenes and incorporating significant amounts of succinic acid [7].

Classes Ia and *Ib* usually involve *trans*-communic isomer acid, which has a lateral chain with a double conjugated bond, a double exocyclic bond between the carbon 8 and 17, and a carboxylic group in carbon 19 (Fig. 2) as the most relevant functional groups.

Regardless the attempt of simplification through this classification, it is important to highlight that fossil resins are not simple polymers formed exclusively by these terpenes linked, but rather a form of macromolecule structure formed as the result of a cross linking process of these terpenes with others compounds present in smaller proportion in the original resins forming after a long process of sedimentation and diagenesis.

Fossil resins formation involves the chemical alteration over millions of years of all the components present in the resin exudates (mainly linear and cyclic terpenes) as consequence of several factors such as temperature, pressure, radiation, water and oxygen to name a few. The reaction mechanism proposed in the literature involves two main stages [8,9]: (a) Initial polymerization-like process (forming a form of macromolecule) between the conjugated double bonds of the side-chain olefin, leading mainly to 14,15-polylabdatrienes through a 1-2 addition reaction to conjugated double bond in *trans*-labdatriene isomers, followed by prolonged exposure to sun and air (among others conditions) resulting in semi-fossil resins known as Copal, (b) Maturation resulting from intramolecular reactions, e. g. isomerizations, cyclization and co-polymerizations, leading to older fossil resins known as ambers. A clear signature of this process is the loss of the exomethylene group C8-C17 (exocyclic base).

These reactive routes have rarely been studied due to their complexity and existing studies have focused on the geological conditions *i.e.*, temperature, pressure, radiation, atmospheric composition, presence of water, sedimentation or diagenesis (i.e. glauconite or blaue Erde) as possible causes of reactivity [10,11,12].

Most of these studies are based on pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) on crude fossil resins [12]. These works serve generally not for simulation of fossilization path but rather for the purpose of recognition of complex macromolecules in the resin structure, by analysis of thermally obtained fragments.

Vibrational spectroscopy (both IR and Raman) have been used for a detailed analysis of the structural characteristics of fossilized resins [13, 14, 15, 16]. Beck [17] and Grimalt *et al.* [18] analyzed by IR spectroscopy a series of ambers and resins from different locations and geological age. They identified a clear and progressive loss in olefinic bonds and decrease of functionalized products with the age of the sample. Lyons *et al*. [19] studied the differences between semi-fossil resins (modern as Copals) and ancient fossil resins from the southern hemisphere. These authors found spectral differences between modern and fossil resins in those bands involving the exomethylene group, while maturation did not lead to noticeable changes in the intensity of some characteristic bands.

We also found several attempts to artificial maturation of amber by temperature, using infrared spectroscopy as characterization technique. For instance, La Mède amber was subjected by Guiliano *et al.* [20] to thermal treatment at 60 ℃ during several days. A progressive decrease of the bands assigned to the exocyclic bond was observed, until their total disappearance after 92 days. Murae *et al.* [21] found that decarboxylation is the major reaction path for the thermal structural alteration. Changes in the exomethylene group started at ca. 250 ℃ and are completed by ca. 300 ℃, and the relative absorption of the carboxylic group decreased linearly up to 400 ℃, although the loss in intensity of the OH stretching band is not as pronounced as other spectral features.

Rottländer [22] reconstructs the structures of fossil resins analysing the effects of temperature on the abietic acid, the main component of resin acids of the genus *Pinus* (conifers from the family *Pinaceae*), when it was thought that these types of resins had been the precursors of ambers. Although later, the classification of Anderson *et al.*, established that the labdanes, coming from resins of the conifers of the genus *Agathis* (family of *Araucariaceae*), had been the basic constituent of the fossil resins *Class I*. the Rottländer's work could be a good starting point to illustrate the structural model that takes place in the heating of communic acids.

Indeed, Mills et al [5], by analyzing the composition of the soluble and insoluble fractions of Baltic amber by capillary gas chromatography-mass spectroscopy, concluded that the polymerization and cross-linking processes of labdatrienes did not need drastic conditions to occur, but rather normal thermal reactions as consequence of the non-equilibrium proportions of the isopimaradine, dihydroagathates and abietic acid present in their analysis. Therefore, their results emphasize the possibility of modeling amber structure through the thermal induced reactivity of the communic acids.

While most existing studies about fossil resin formation are based in the analysis of crude material, here we propose to follow the thermal evolution of a pure terpene precursor (*trans*-communic acid) using IR spectroscopy and Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) as complementary techniques. Being aware the limitation of simulating the fossil resin formation in the laboratory, our aim is to provide evidences of the chemical changes that may occur in the natural fossilization by analyzing the thermal induced reactivity both in oxygen and inert (N_2) atmospheres of the main component of the *Class* I resins.

2. Experimental details

2.1. Extraction of the pure sample

Trans-communic acid is not commercially available and was extracted from cypress berries existing in the Iberian Peninsula (*Cupressus Sempervirens L.*) [23]. Communic acids were extracted with hexane in a Soxhlet extractor from a purée made from the harvested berries. The resulting extract was defatted by low-temperature precipitation. The fat-free extract was dissolved with a series of solvents such as methyl *t*-butyl ether, methanol/benzene (1:4), etc. A chromatographic separation over silica gel impregnated with 20% silver nitrate was required to separate the isomers. The purity of the communic acids was assessed by ^{1}H-NMR spectroscopy using a Bruker ARX 400 (1H 400 MHz) spectrometer. The data obtained for the *trans*-communate sodium form were: 6.25 ppm (1H, dd, J_1 = 12, J_2 = 16 Hz), 5.36 ppm (1H, t, J= 6.8 Hz), 4.96 ppm (1H, d, J = 16 Hz), 4.81 ppm (1H, J= 12 Hz), 4.78 ppm (1H, s), 4.40 ppm (1H, s), 1.69 ppm (3H, s), 1.18 (3H, s) y 0.59 (3H, s).

2.2. Infrared spectra measurements and spectral assignment

Samples were thoroughly ground with exhaustively dried KBr to prepare pellets by compression under vacuum in a Graseby-Specac 15.011 15 ton hydraulic press. IR spectra were measured using a Thermo Scientific Nicolet Magna IR-750 Spectrometer, with a high-performance DTGS-KBr detector mounted on pre-aligned, pinned-in-place baseplate for optimal sensitivity. This device includes a KBr beamsplitter and an Ever-Glo (mid-IR to far-IR) source. The OMNIC software package was used to control the spectrometer and the acquisition parameters (128 averaged scans averaged at 4 cm^{-1} spectral resolution). Background correction was applied in each measurement.

Two types of temperature experiments were conducted. The first was to perform IR measurements by heating the sample to different temperatures. Subsequently, at each step the sample was allowed to cool down to room temperature before recording the IR spectrum. The experiments were carried out up to 340 ºC, since above that temperature there was visual evidence of the onset of burning of the samples. It was not necessary to control the humidity conditions during the experiments.

In Fig. 3 we can see the different residues recovered at room conditions after the thermal treatment, what we have labeled as "artificial fossil resin analog". As temperature increases we can observe the usual yellow-orange-brown color associated with fossil resins. At 340 ºC, we recover an analog with black appearance, indicative that at higher temperatures it is produced the burning of the samples.

2.3. Differential Scanning Calorimetry (DSC) measurements

DSC measurements were carried out with a TA Instruments DSC, model Q10, connected to a RCS cooling unit. Tightly sealed aluminum pans were used under dry nitrogen flow at 50.0 mL min^{-1}. A MT5-Mettler microbalance was used to monitor the weight of the samples with an uncertainty of 0.001 mg. The calorimeter was calibrated in temperature using standard samples of In and Sn, supplied by TA (purity >99.999% and >99.9%, respectively), and of benzoic acid (purity >99.97%), supplied by the former NBS, and in enthalpy with the In and Sn standards already described. The DSC experiments consisted in a first heating run from 20 ºC up to 250 ºC, followed by a cooling

down to 20 ºC to check the absence of irreversible processes, and a second heating run up to 340 ºC.

2.4. Thermo-Gravimetric Analysis (TGA) measurements

TGA measurements were carried out using Delta Series TA-SDT Q600 in nitrogen flow (100 mL min⁻¹) at a heating rate 5 ºC min⁻¹ between 40 and 275 ºC, and 3 ºC min⁻¹ between 275 and 340 ºC, with Platinum crucibles.

3. Results and Discussion

3.1. Spectral assignment of the vibrational modes of *trans*-communic acid

The spectral assignment of the vibrational modes of *trans*-communic acid is summarized in Table 1. It was performed from the experimental Raman and IR spectra [24] with the aid of Density Functional Theory (DFT) calculations at the B3LYP level using a cc-pVDZ basis set included in the GAMESS package [25], previous assignments for similar compounds [26] and different fossil resins [16-18]. For sake of clarity, we mainly present the modes related with stretching of double bonds of these molecules, with special attention to bonds C=C and C=O, besides bending and stretching of C-H bonds linked to these double bonds. This assignment can be used as a good basis to interpret the vibrational spectra of similar *Class I* fossil resins, because most of them derive form *trans*-communic acid cross-linked polymers.

3.2. DSC and TGA experiments

DSC analysis between 100 and 230 ºC were plotted in Fig. 4. Because this compound is unstable, no thermal data exist for its acid form, and only thermal data for its esterified form is found in the literature [27,28]. In Fig. 5, combined results of DSC/TGA are depicted. Our DSC results indicate that the melting point of *trans*-communic acid is 123 ºC. No evidence of glass transition (T_g) before this melting point was found. At 130 ºC a slow exothermic process begins and ends up at 170-175 ºC. The changes suffered by the *trans*-communic acid within this temperature range may be related to those occurring during the initial polymerization of fossil resins at natural conditions. In Fig. 5, the combined combining DSC/TGA analysis show that a glass transition between 175 and 180 °C and that another sluggish exothermic process appears above 175 ºC. This exothermic process is continued up to 340 ºC and seems to reproduce the polymerization by maturation of *Class Ib* fossil resins, in agreement with the observations of Clifford and Hatcher [8].

3.3. Infrared spectra of *trans*-communic acid heated at different temperatures

In a previous work [23], we analyzed the temperature behavior of *trans*-communic acid using Raman spectroscopy, and we concluded that the reactivity changes occurred at 130 ºC may mimic those to the natural polymerization like process. However, the potential reactivity of *trans*-communic acid at higher temperatures could not be probed due to the intense fluorescence of the residue above 170-175 ºC.

The present IR experiments allowed us to monitor such potential changes at temperatures up to 340 ºC. We have analyzed the evolution of the more characteristic IR bands of *trans*-communic acid with increasing temperature, paying special attention to

those modes involving double bonds (conjugated and exocyclic C=C) and the carboxylic acid group. In Figures 6 and 7, we show the spectra measured at selected temperatures, which have been normalized to the most intense band (in absorbance) for each measurement in order to better compare the spectral changes found. In Fig. 8, we compared two selected spectra as measured to show the broadening and loss of relative intensity in most spectral features at the higher temperature. Such behavior is indicative of a massive polymerization-like (maturation) process.

From the results of Fig. 6, we observe the following spectral characteristics (all referred to the IR spectra measured at 25 ºC): symmetric and anti-symmetric C-H stretches, involving in double bonds conjugated [v_{as} ($C^{14}H=C^{15}H_2$ conjugated) at 3093 cm^{-1} and v_s ($C^{14}H=C^{15}H_2$ conjugated) at 3002 cm^{-1} *sh*] and v ($-C^{12}H=C^{13}R-$) at 3036 cm^{-1} show a weak IR absorbance, but these modes have disappeared at 180 ºC, thus suggesting that the conjugation in side-chain has been lost in the residue obtained after heating. The modes v_{as} (3078 cm^{-1}) and v_s (2986 cm^{-1}) of the exocyclic double bond $C^8=C^{17}$-H remain up to 210 ºC, but they are not observed above 290 ºC. At the highest temperature studied, 340 ºC, the most prominent spectral feature is that centered around 3430 cm^{-1} (v(OH), Figs. 6 and 8). The C-H stretching modes of sp^3 carbons (Fig. 6): [v_{as} (CH_3) at 2964 cm^{-1}, v_{as} (CH_2) at 2952 cm^{-1}, v_s (CH_3) at 2935 cm^{-1}, v_s (CH_2) at 2905 cm^{-1}, v (R_3C^5H bridge) at 2870 cm^{-1} and v (R_3C^9H) at 2845 cm^{-1}], increase their width and overlap with increasing temperature.

The most important changes were observed in the spectral region related to double bonds stretching (Fig. 7). The v(C=O) mode at 1693 cm^{-1} is the strongest peak in the IR spectrum. This frequency value is lower than those typically observed in other carboxylic acids due to the existence of carboxylic dimers in the crystal. In any case, this mode decreases its intensity with increasing temperature, and develops a shoulder at 1735 cm^{-1} above 180 ºC. At 340 ºC an additional shoulder appears at 1772 cm^{-1} together with another new broad band at 1618 cm^{-1}. The 1735 cm^{-1} shoulder might be indicative of the formation of anhydride forms (or even lactones and/or carboxylate ester forms, although the appearance of esters is unlikely because alcohols are absent in the initial reactive). This suspicion is confirmed by the loss in weight observed in our TGA results, which can derive from intramolecular dehydration. In any case, our results suggest a loss of carboxylic dimerization in the fossil resin analog residue obtained by polymerization of the *trans*-communic acid along the heating treatment.

The v_{as}(C=C conjugated) mode centered at 1606 cm^{-1} has almost disappeared at 180 and 210 ºC. On the other hand, the v_s(C=C conjugated) mode centered at 1643 cm^{-1} do not change its intensity but broadens and shifts towards higher frequencies, overlapping with the v($C^8=C^{17}$ exocyclic) mode at 1650 cm^{-1} as the temperature treatment proceeds. This observation can be attributed to a loss of conjugation in the fossil resin analog created during the initial polymerization-like process. This doublet is barely visible at 290 ºC, and no evidence is found in the sample heated at 340 ºC, indicating also the loss of the exocyclic bond.

It is also interesting to note the existence of a broad band at 927 cm^{-1}, which is characteristic of carboxylic acids with hydrogen bonds, $\gamma_{o.o.p.}$ (OH···H). This band disappears with increasing temperature, indicating the loss of carboxylic dimerization.

Finally, the $\gamma_{o.o.p.\ wagging}$($R_2C^8=C^{17}H_2$) mode at 892 cm^{-1}, which is among the most characteristic IR vibrational modes of *Class I* fossil resins, is observable up to 210 ºC, indicating that the exocyclic bond is present at least up to this temperature. The $\gamma_{o.o.p.\ twisting}$($-HC^{14}=C^{15}H_2$) at 987 cm^{-1}, is absent above 180 ºC due to the loss of conjugation.

Summarizing, our IR results indicate a progressive decrease in the absorption of the bands related to the carboxylic group, the olefinic and exocyclic bonds, and in v(OH).

However, some spectral changes observed in our experiments, even at the highest temperature (340 ºC), slightly differ from previous observations. For instance, Lyons *et al*. [19], in their comparative study between modern and fossil resins, stated that the bands in the aliphatic and double bonds spectral regions do not experience a drastic reduction in intensity, in contrast to our present observations. However, our results in the low and high temperature regimes are compatible with the observations of Lyons *et al.* for the relative intensities of the exomethylene bands found in less ancient (as copals) and ancient fossil resins (as amber), respectively.

3.4. Comparison of heating of *trans*-communic acid in the oxygen atmosphere *vs.* heating in inert atmosphere

In the Fig. 9, we compare the FTIR spectra of *trans*-communic acid at 25 ºC after heating the sample at selected temperatures (230 and 340 ºC). Heating runs were carried out under either oxygen or inert (nitrogen) atmospheres.

The IR spectra corresponding to the samples heated to 230 ºC do not show major differences, in clear contrast to those corresponding the sample heated to 340 ºC. With oxygen it is observed a larger degradation, thus confirming the strong effect of oxygen in the loss of the carboxylic group and in the maturation process of *trans*-communic acid.

4. Summary and Conclusions

In this work we used IR spectroscopy, combined to DSC and TGA analyses, to study the temperature-induced transformations of *trans*-communic acid, which is considered one of the main precursors for fossil resins *Class Ia* and *Class Ib*.

In general, our thermal induced reactivity results between 130-175 ºC confirm the two-stage maturation scheme proposed by Clifford and Hatcher [8]. From the combined DSC/TGA results, we conclude that chemical changes that took place in the *trans*-communic acid between 130 and 175 ºC are similar to those reported by the polymerization-like process, whereas the changes associated with the real maturation process are similar to the thermal changes observed between 180 and 340 ºC.

Our results confirm the loss of conjugation in the side-chain groups once the analog of fossil resin is formed by initial polymerization around 180 ºC. This analog of fossil resin losses the characteristic broad band of carboxylic acids having hydrogen bonds, $\gamma_{o.o.p.}(OH\cdots H)$, thus indicating loss of carboxylic dimerization. In relation to the $\gamma_{o.o.p.wagging}$ ($R_2C^8=C^{17}H_2$) mode at 892 cm^{-1} (the most important IR mode of fossil resins to date the archaeological age of *Class I* fossil resins), its intensity decreases significantly above 290 ºC. At this temperature the band around 1645 cm^{-1} has significantly reduced its absorbance as well, which reflects the loss of the exocyclic bond.

This allows us to conclude that the *trans*-communic acid suffer a maturation-like reaction above this temperature. These chemical changes are in agreement with the natural maturation schemes proposed in the literature. The severe maturation-like process observed in our experiments at 340 ºC disagrees with the existing studies of fossil resins considering different locations and geological ages. This very likely means that in this work the samples, subjected to stronger heating conditions, undergo through different chemical reactions that those leading to the formation of fossil resins in real natural environments.

Another important result of our study to be considered is the effect of the presence of O_2 in the maturation of *trans*-communic acid, which leads to a faster loss of carboxylic group.

In summary, our results provide key information for understanding the polymerization/maturation process of communic acids and provide a solid basis to interpret similar reactions related to the formation and evolution of amber and others fossil resins using IR spectroscopy. Moreover, this work might also serve as a reference for distinguishing amber from less matured resins as copal, determining the local origin of archaeological fossilized resins, identifying imitations or falsifications in jewelry, and other forensic applications.

Acknowledgments

FIGURES
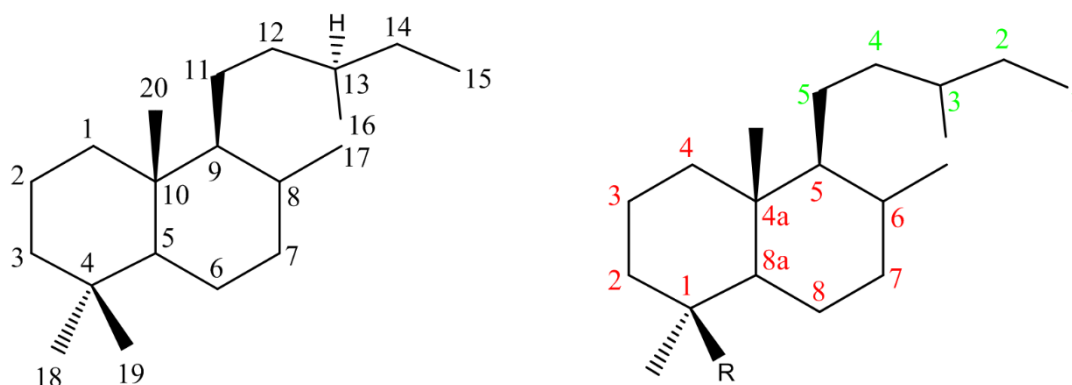
**Fig. 1**. Left: Labdane skeleton with standard numeration. Right: Labdane skeleton with IUPAC nomenclature.
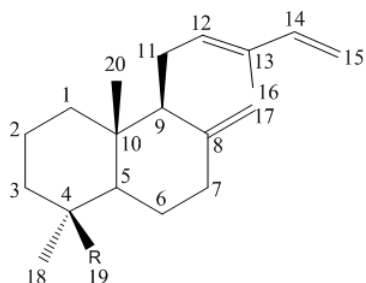
Conjugated double bonds *trans*-.
R = CH₃, *trans*-biformene
R = CH₂OH, *trans*-communol
R = COOH, *trans*-communic acid
R = COOMe, methyl *trans*-communate

Fig. 2. Hydrocarbon, alcohol, carboxylic acid, and ester Labdatriene, with standard numeration. Arrangement of conjugated double bond in the *trans*-conformation.
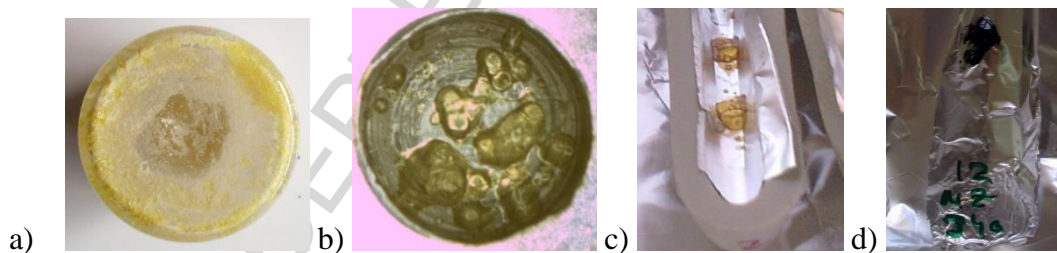

Fig. 3. a) *trans*-Communic acid at 25 ℃ enclosed in argon atmosphere; b), c) and d) samples recovered of the same terpene, but first heating up to 180, 290 and 340 ℃ respectively, and then cooling down to 25 ℃.
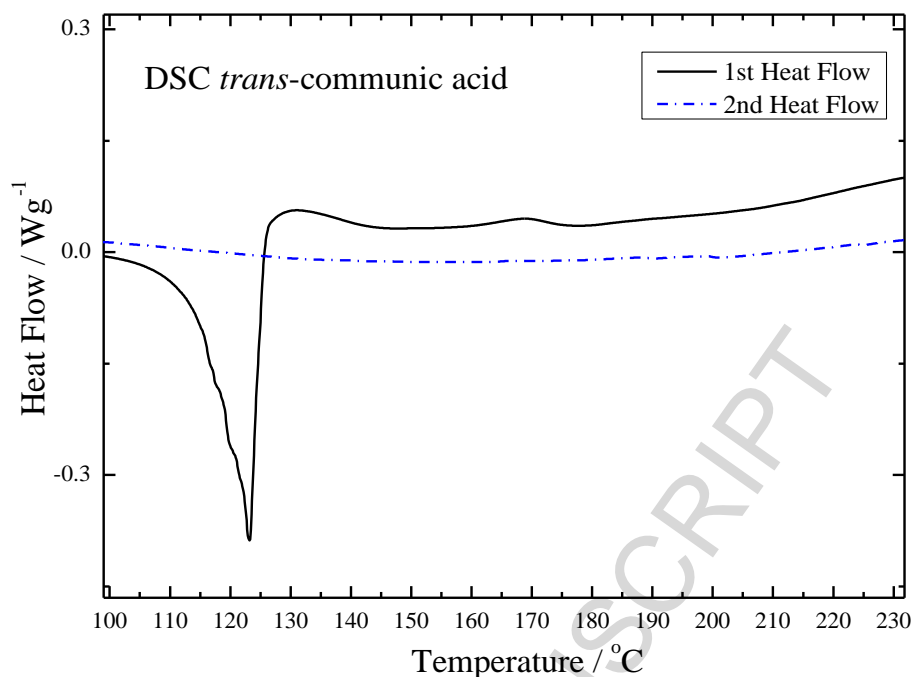
Fig. 4. DSC of *trans*-communic acid between 100 and 230 ºC.
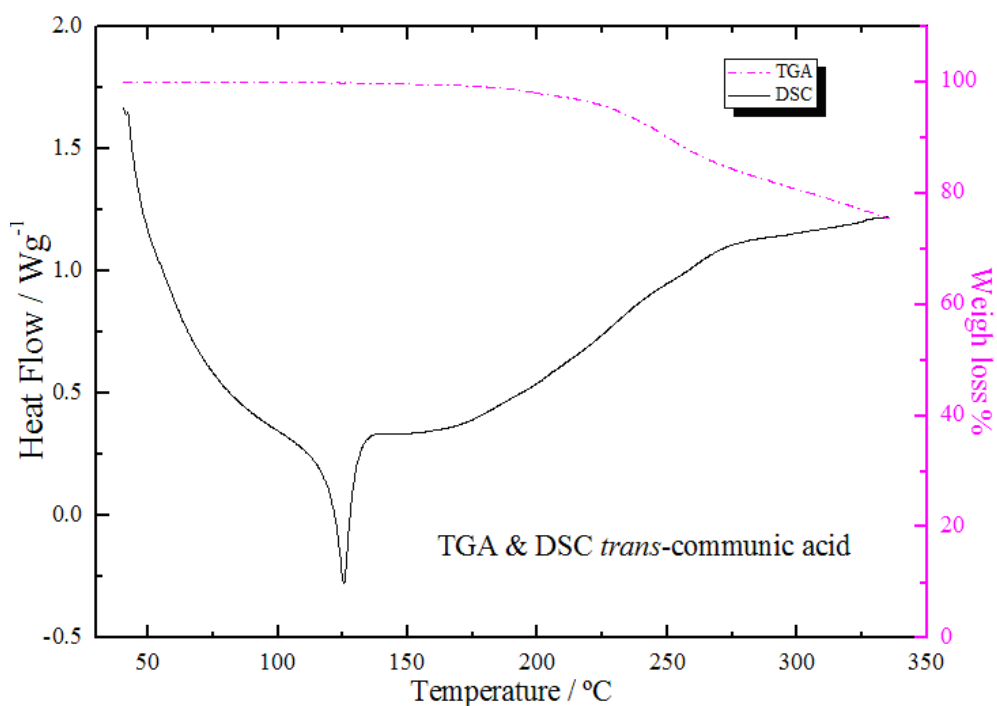
Fig. 5. TGA (dash line) and DSC (dot line) of *trans*-communic acid between 40 and 340 ºC. [Note: slope changes in both measurements at 275 ºC are due to changes in heat flux along the experimental runs].
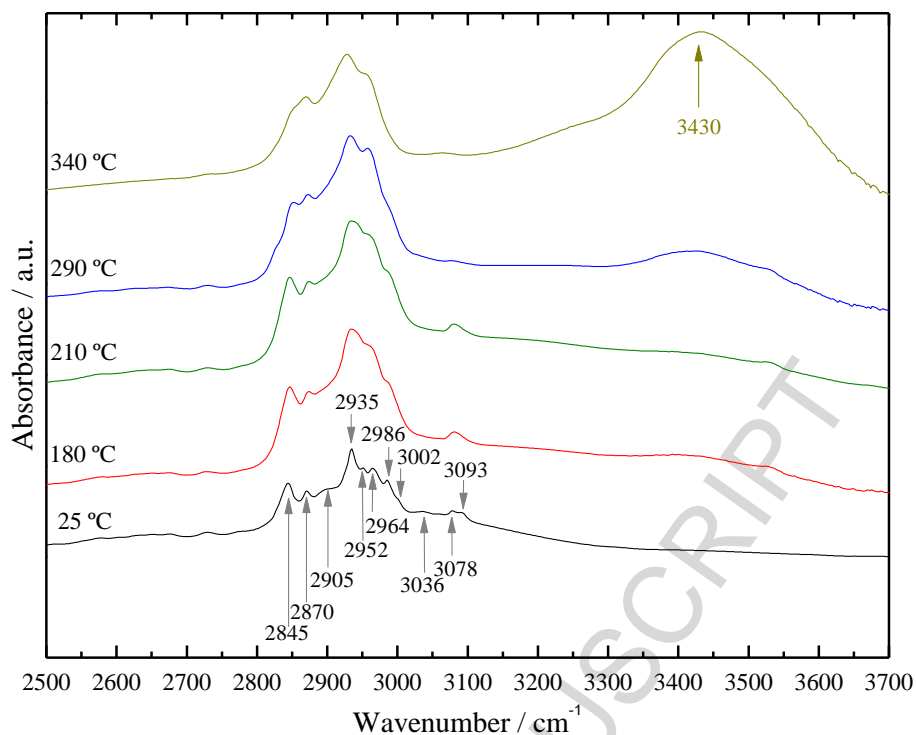
Fig. 6. FTIR spectra (region 2500-3700 cm^{-1}) of *trans*-communic acid measured at 25 ℃, the sample was previously heated to the indicated temperatures.
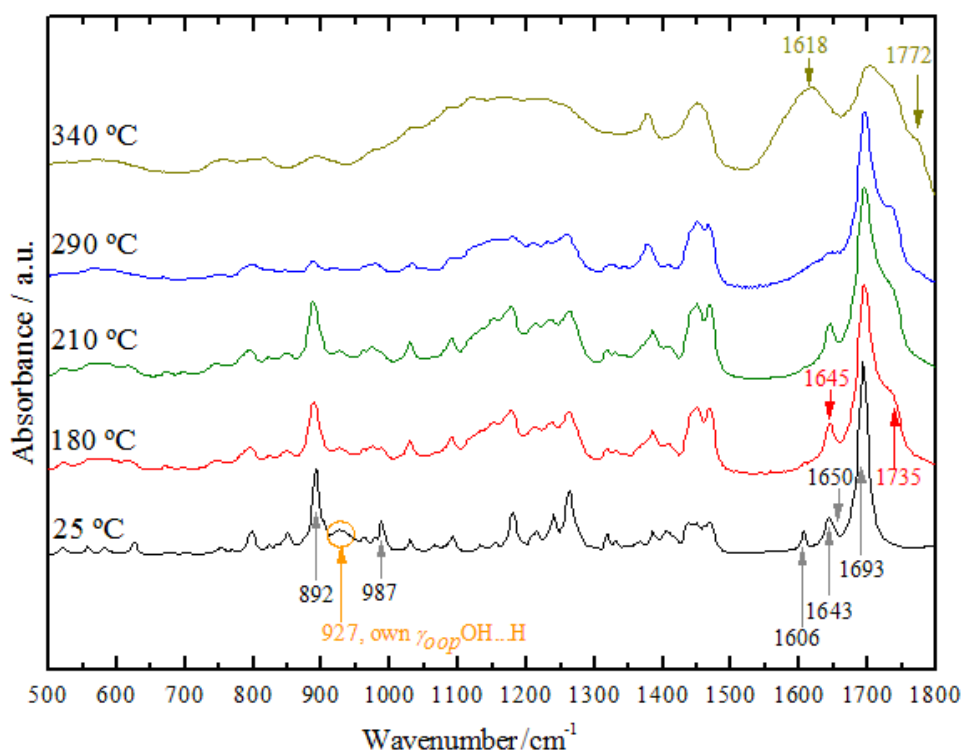
Fig. 7. Normalized FTIR spectra (region 500-1850 cm^{-1}) of *trans*-communic acid recorded at 25 ℃. The sample were previously heated to the indicated temperatures and cooled down to room conditions for spectroscopic measurement.

11
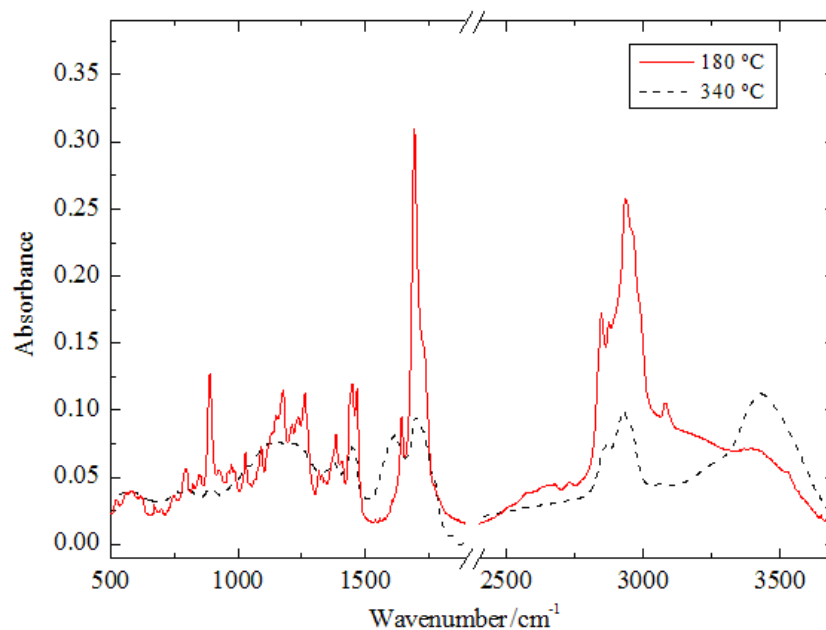
Fig. 8. Comparison of two selected FTIR spectra form Fig. 6 (not normalized).
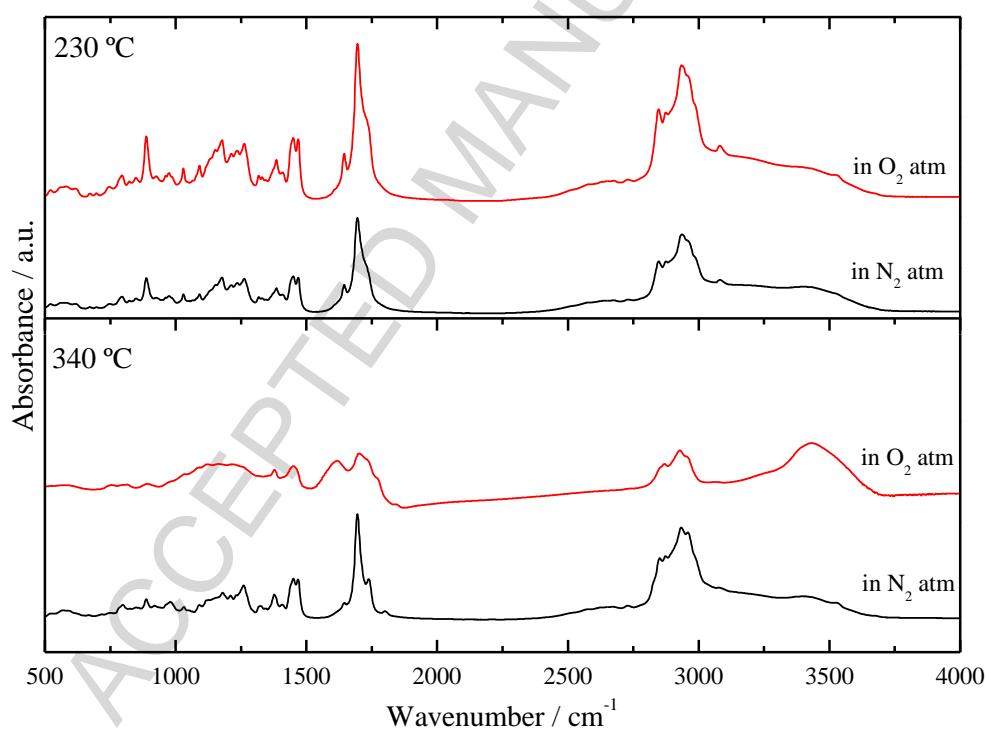
Fig. 9. FTIR spectra of *trans*-communic acid recorded at 25 ºC. The samples were exposed to different ambient conditions (N_2 or O_2 atmosphere) and heated to the indicated temperatures before cooling down to room conditions for spectroscopic measurement.

Table 1. Vibrational assignment of the experimental infrared spectrum, for the isomer *trans*-communic acid at 25 ºC [24] without any kind of treatment in temperature. [*as: asymmetric; s: symmetric: i.p.: in plane; o.o.p.: out of plane; R: organic side chain; vw: very weak w: weak; m: medium; s: strong; vs: very strong; sh: shoulder; br: broad; vbr: very broad*].

trans-Communic acid	
Mode	**Infrared Wavenumber (cm^{-1})**
ν (OH)	3430 vbr
ν_{as} (C^{14}H=C^{15}H$_2$ conjugated)	3093 w
ν_{as} (C^8=C^{17}H$_2$ exocyclic)	3078 w
ν (-C^{12}H=C^{13}R-)	3036 w
ν_s (C^{14}H=C^{15}H$_2$ conjugated)	3002 vw sh
ν_s (C^8=C^{17}H$_2$ exocyclic)	2986 m
ν_{as} (CH$_3$)	2964 m
ν_{as} (CH$_2$)	2952 m
ν_s (CH$_3$)	2935 s
ν_s (CH$_2$)	2905 w
ν (R$_3$C^{5}H bridge C)	2870 m
ν (R$_3$C^{9}H)	2845 s
ν (C=O)	1693 vs
ν (C^8=C^{17} exocyclic)	1650 sh
ν_s (C=C conjugated)	1643 m
ν_{as} (C=C conjugated)	1606 m
$\delta_{i.p.}$ (R$_2$C^8=C^{17}H$_2$) scissoring & (-C^{7}H$_2$)	1405 w sh
$\delta_{i.p.}$ (-HC^{14}=C^{15}H$_2$ conjugated scissoring) & R$_2$C^8=C^{17}H$_2$ exocyclic)	1384 w
$\delta_{i.p.}$ (-C^{12}H=C^{13}R-)	1365 w
$\delta_{i.p.}$ (C-O-H)	1320 m
ν (C-O)	1260 s
$\gamma_{o.o.p.}$ (C-O-H)	1092 w
$\gamma_{o.o.p.}$(-HC^{14}=C^{15}H$_2$) twisting + $\gamma_{o.o.p.}$ (-HC^{12}=C^{13}R-)	987 m
$\gamma_{o.o.p.}$ (OH...H)	927 br
$\gamma_{o.o.p.}$(R$_2$C^8=C^{17}H$_2$) wagging	892 s

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Highlights

- The *trans*-communic acid (terpene derivative) was subjected to controlled temperature treatment, focusing on temperature only as a possible helpful agent causing the maturation of fossil resins.
- Infrared spectroscopy, DSC and TGA are used to follow the process.
- Results are compared with maturation schemes proposed in literature for fossil resins.
- An "artificial initial polymerization" is proposed that occurs between 135-170 ℃.
- An "artificial maturation polymerization" is proposed that occurs around 180-340℃.