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Pressure as driving force in the formation of Fossil Resins: Pressure Induced Changes in *trans*-Communic Acid studied by Raman Spectroscopy

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Abstract. The main purpose of this study is to provide spectroscopic evidence of possible chemical pathways in the formation of fossil resins under high pressure conditions. In this work, we have studied *trans*-communic acid (majority precursor compound in resinites) under high pressure conditions by using a sapphire anvil cell. Raman spectra were measured at atmospheric pressure up to 8 GPa (at room temperature). Slight changes were observed in the spectra. Furthermore, the recovered sample after pressure release was analyzed by FTIR. Our results are not conclusive about a possible chemical pathway of polymerization induced by pressure.

1. Introduction

Fossil resins are organic gemstones which have survived up to now. In general, they derive from natural terpene-based polymers, and are classified in five classes. *Class I* is the most important; its members are composed by polymerization of labdanic acid monomers, primary communic acids (labdatriene diterpenes) [1-3]. From them, Baltic Amber is the most well-known *Class I* resinite.

In Figure 1, we schematize the principal labdatriene isomer in his acid form, i.e. *trans*-communic acid [4], which is the main precursor for a large majority of *Class I* resinites.

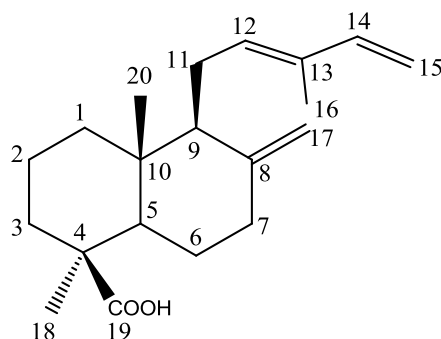


Figure 1. *trans*-Communic acids.

The reactive processes that took place in the formation of fossil resins are barely studied due to their complexity. Current studies conclude that maturing reactions or reactivity schemes of the different *Class I* resinates, seem to occur in two polymerization stages [5,6].

The first suggested step consists of an initial polymerization between the conjugated double bonds of the side-chain olefin (1-2 addition to conjugated double-bonds in *trans*-labdatrienes isomers). Later in the ages, polylabdanoid resinates continue with a more specific reaction resulting in depletion of the C8-C17 exomethylene (exocyclic bond), due to intramolecular cyclation reactions, intramolecular polymerization, among others.

These processes took place throughout ages until formation of fossil resins. Several studies are focused on how the geological environment conditions such as temperature [7], radiation or atmosphere compositions [8], act on trees exudation. However, there is no study considering the pressure as geological condition, even though Baltic Amber samples have been found in the Baltic Sea depths, as well as other resinates buried in under the Earth's surface [9].

Baltic Sea is 57 m depth, on average, and its maximum depth is 459 m. Those are not significant depths in order to generate a substantial high pressure in geological terms, as it can go into the depths of the Pacific Ocean. Nevertheless, fossil resins have been buried under the sea for millions of years. From this point of view, pressure should be taken into account as a formation variable.

In this work, we have studied *trans*-communic acid under pressure conditions by using a sapphire anvil cell (SAC), in order to identify if pressure is an important geological agent in the formation of the fossil resins. Firstly, Raman spectra of the pressurized samples were collected, from room pressure up to 8 GPa. Then FTIR spectra of the recovered sample were recorded at ambient conditions.

2. Experimental

The high pressure experiments of this work were carried out at room temperature in a 350 μm culet SAC. The pressure was determined by Raman spectroscopy using the linear variation of the diamond fundamental phonon [10]. The sample was loaded together with a diamond chip, into a 100- μm -diameter hole drilled on a 200- μm -thick golden gasket pre-indented to 40 μm . In addition to the chip diamond, a ruby chip was loaded as possible alternative to measure the pressure [11]. The *trans*-communic acid itself was used as pressure-transmitting medium.

Raman spectra of the *trans*-communic acid were recorded on a confocal micro-spectrometer (B&W Tek VoyageTM, model BWS435-532SY). The spectrometer is coupled to an Olympus BX51 microscope, which allows us to focus the beam spot (~ 5 μm) onto the sample to register spectra. Excitation is provided by a solid-state laser operating at 532 nm. The spectral range available is 100-3750 cm^{-1} with spectral resolution of about 4 cm^{-1} . But we shall focus on the spectral ranges between 600-1800 and 2800-3200 cm^{-1} . The scattered light is collected on backscattering configuration using a 20x long working-distance objective. The detector consists in a backthinned CCD (Hamamatsu S10141-1107S) thermoelectrically cooled at -20 $^{\circ}\text{C}$ with 2048 \times 122 pixels. A ChameleonTM CMLN-13S2C digital camera is used for optical observation. Previously to the temperature study, the laser power influence on the sample was carefully analyzed. All the spectra were registered using laser excitation power of *ca.* 2 mW to avoid unwanted heating.

FTIR spectrum of the *trans*-communic acid was recorded in a Spectra-Tech IR-Plan microscope for reflected light microspectrometry. The microscope uses a 15x IR reflecting lens with Cassegrain optics to focus the infrared beam onto the sample and it is equipped with a liquid-N₂ cooled MCT-A detector.

The molecule used in this study is a pure isomer of communic acid: *trans*-communic acid. Since it is not commercially available, their extraction was carried out from *Cupressus* and *Juniperus* (*Cupressus Sempervirens L.*, *Juniperus Communis L.* and *Juniperus Oxycedrus*) [12,13]. In order to validate the purity of the communic acids ¹H-NMR spectroscopy was employed to characterize the *trans*-communic acid [7].

Spectral assignment of the vibrational modes of *trans*-communic acid is based on both, the existing spectral assignments for this molecule [7, 8], and the assignments of different fossil resins found in the literature [14-17].

3. Results and discussion

We have studied *trans*-communic acid under high pressure conditions by using a sapphire anvil cell. Raman spectra were measured at atmospheric pressure up to 8 GPa (at room temperature). Furthermore, when the pressure was released, the recovered sample was analyzed by FTIR.

The study of these spectra is focused on the next spectral regions: a) C-H stretches, and b) modes involving double-bond stretches, with special attention those involving C=C and C=O moieties, and C¹⁷-H exomethylene wagging (exocyclic double bond).

3.1. Pressure Induced Changes in *trans*-Communic Acid studied by Raman Spectroscopy.

Raman spectra at different pressures of *trans*-communic acid show the following results:

3.1.1. C-H stretches región. The vibrational modes present in C-H stretches region (Figure 2) have only been measured until 0.4 GPa, due to the fluorescence background and the weak intensity of these modes above this pressure value. The studied Raman modes are: $\nu(\text{R}_3\text{C}^9\text{H}) = 2847 \text{ cm}^{-1}$; $\nu(\text{R}_3\text{C}^5\text{H}$ bridge C) = 2870 cm^{-1} ; $\nu_s(\text{CH}_2) = 2908 \text{ cm}^{-1}$; $\nu_s(\text{CH}_3) = 2936 \text{ cm}^{-1}$; $\nu_{as}(\text{CH}_2) = 2952 \text{ cm}^{-1}$; $\nu_{as}(\text{CH}_3) = 2963 \text{ cm}^{-1}$; $\nu_s(\text{C}^8=\text{C}^{17}\text{H}_2$ exocyclic) = 2986 cm^{-1} ; $\nu_s(\text{C}^{14}\text{H}=\text{C}^{15}\text{H}_2$ conjugated) = 3002 cm^{-1} ; $\nu(\text{-C}^{12}\text{H}=\text{C}^{13}\text{R-}) = 3036 \text{ cm}^{-1}$; $\nu_{as}(\text{C}^8=\text{C}^{17}\text{H}_2$ exocyclic) = 3079 cm^{-1} ; $\nu_{as}(\text{C}^{14}\text{H}=\text{C}^{15}\text{H}_2$ conjugated) = 3094 cm^{-1} .

Only slight changes have been observed around 2850-3100 cm^{-1} at 0.4 GPa (Figure 2). This region involves the -CH₂- and -CH₃ stretching modes. The detected changes consist of a broadening and shifting of these peaks to higher wavenumbers with pressure. That could be related to some slight conformational changes in the molecule. No evidence of chemical reaction is observed.

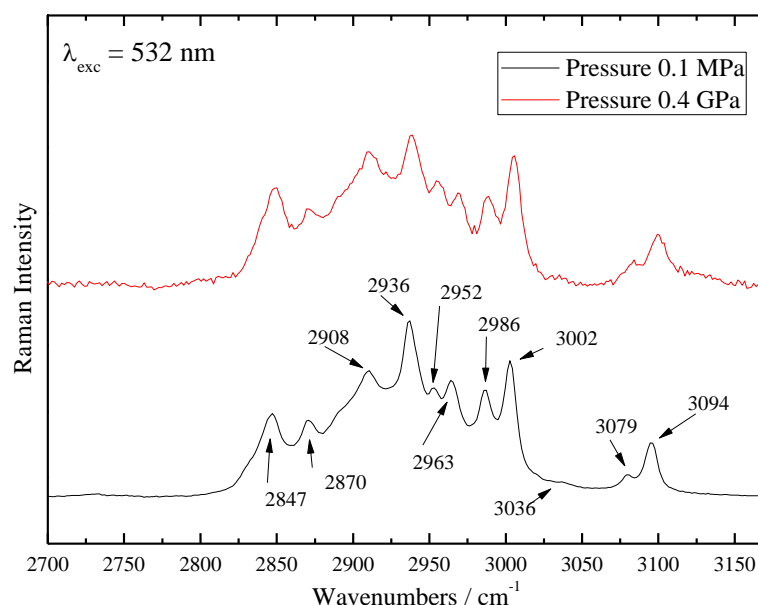


Figure 2. Enlarged Raman spectra of *trans*-communic acid at atmospheric pressure and 0.4 GPa.

3.1.2. Double-bond stretches (C=C), C-H bendings and C-O stretch region. Raman spectra in this region (Figure 3) were measured from atmospheric pressure up to 8 GPa. We have followed the gradual change of the most characteristic Raman bands of *trans*-communic acid that involve carbon-carbon double bonds C=C (conjugated and exocyclic), with pressure. In general, these modes decrease in intensity as the fluorescence background increases, becoming weak bands.

In this case as well, the previous mentioned factors, band shifting and band broadening, make arduous to follow their evolution pressure.

Despite all these difficulties, we can see how only above 3.3 GPa, the two more characteristic bands $\nu_s(\text{C}=\text{C}$ conjugated) and $\nu_{as}(\text{C}=\text{C}$ conjugated) at 1643 cm^{-1} and 1606 cm^{-1} , respectively, overlap yielding a single broadband.

Other bands, as the $\nu(\text{C}-\text{O})$ at 1294 cm^{-1} or the C-H bendings, do not show relevant changes. Therefore, we can conclude that there is no evidence of chemical reaction.

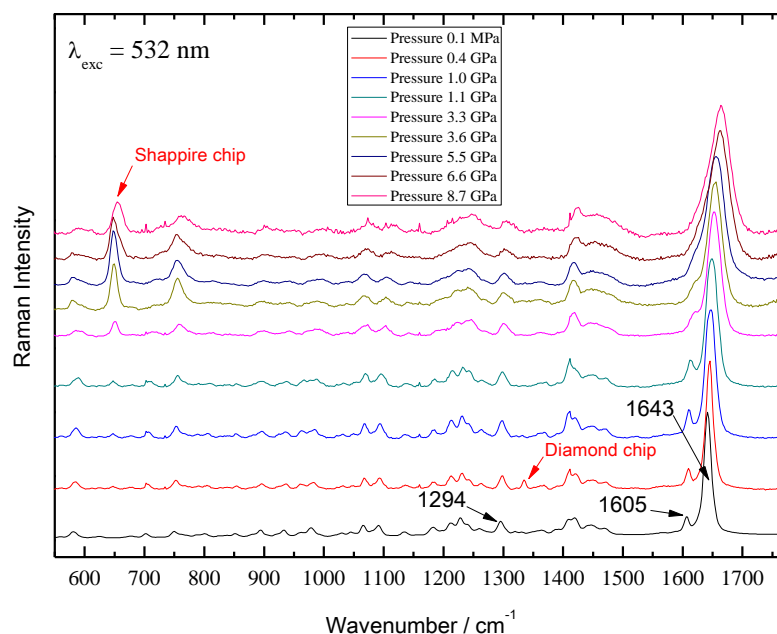


Figure 3. Raman spectra of *trans*-communic acid at selected pressures.

3.2. Pressure Induced Changes in *trans*-Communic Acid recovered by FTIR.

Before the cell opening, we tried to collect the FTIR spectra of *trans*-communic acid inside the SAC at 8.0 GPa (the sample was stabilized during 109 days at this pressure), but due to the small size of the gasket hole and the spectral sapphire window, the results were unsuccessful.

Consequently, we decided to proceed with the opening of the SAC, in order to collect the FTIR spectrum by reflection of the sample recovered placed directly over the anvil surface. The spectrum was recorded on the SAC to prevent sample losing while handling due to small dimensions.

An important detail about the recovered sample is to highlight that no colour changes were observed.

3.2.1. C-H stretches region. Both FTIR spectra of *trans*-communic acid, shown in Figure 4, were measured at atmospheric pressure, but recovered sample (plotted in red), was pressurized at 8.0 GPa during 109 days.

The vibrational modes present in C-H stretching region (Figure 4), do not seem to undergo significant changes except for its displacement towards higher frequencies. The IR studied modes are: $\nu(\text{R}_3\text{C}^9\text{H}) = 2845\text{ cm}^{-1}$; $\nu(\text{R}_3\text{C}^5\text{H}$ bridge C) = 2870 cm^{-1} ; $\nu_s(\text{CH}_2) = 2905\text{ cm}^{-1}$; $\nu_s(\text{CH}_3) = 2935\text{ cm}^{-1}$; $\nu_{as}(\text{CH}_2) = 2952\text{ cm}^{-1}$; $\nu_{as}(\text{CH}_3) = 2964\text{ cm}^{-1}$; $\nu_s(\text{C}^8=\text{C}^{17}\text{H}_2$ exocyclic) = 2986 cm^{-1} ; $\nu_s(\text{C}^{14}\text{H}=\text{C}^{15}\text{H}_2$ conjugated) = 3002 cm^{-1} ; $\nu(-\text{C}^{12}\text{H}=\text{C}^{13}\text{R}-) = 3036\text{ cm}^{-1}$; $\nu_{as}(\text{C}^8=\text{C}^{17}\text{H}_2$ exocyclic) = 3078 cm^{-1} ; $\nu_{as}(\text{C}^{14}\text{H}=\text{C}^{15}\text{H}_2$ conjugated) = 3093 cm^{-1} .

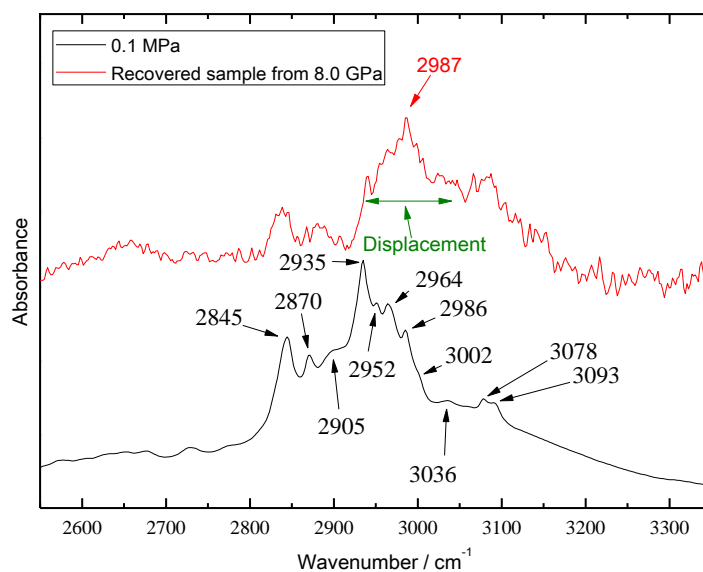


Figure 4. Enlarged FTIR spectra of *trans*-communic acid both at atmospheric pressure, but drawn in red the “Recovered Sample” after pressurizing at 8.0 GPa for 109 days.

3.2.2. *Double-bond stretches (C=O and C=C) and C-H bendings region.* As the previous section, in this new spectral region, both FTIR spectra of *trans*-communic acid (Figure 5) were measured at atmospheric pressure, but one of them (displayed in red) is over a recovered sample after having undergone at 8.0 GPa during 109 days.

We have followed the evolution of the more characteristic IR bands of *trans*-communic acid involving the next modes: $\gamma_{o.o.p.}(R_2C=CH_2) = 892 \text{ cm}^{-1}$; $\nu_{as}(C=C) = 1606 \text{ cm}^{-1}$; $\nu_s(C=C) = 1643 \text{ cm}^{-1}$; $\nu(C^8=C^{17}) = 1650 \text{ cm}^{-1}$; $\nu(C=O) = 1693 \text{ cm}^{-1}$. As well as in the previous region, a band broadening and a displacement of the spectral features until higher wavenumbers with the pressure have occurred.

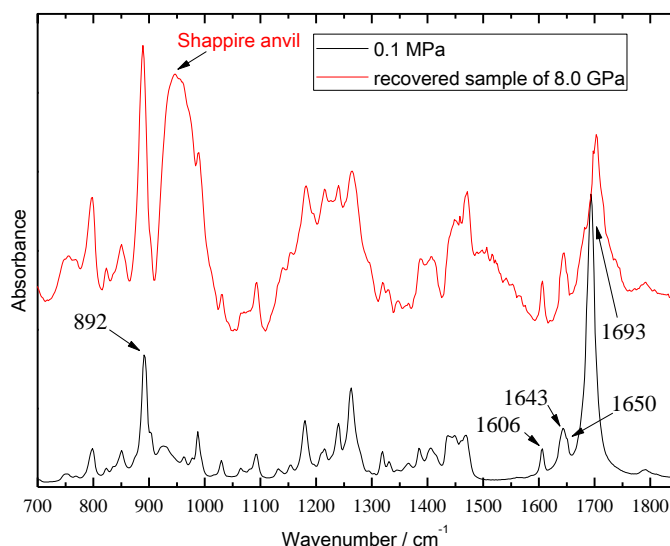


Figure 5. Enlarged FTIR spectra of *trans*-communic acid both at atmospheric pressure, the “recovered sample” (red) was pressurized at 8.0 GPa for 109 days.

4. Conclusions

We have used high pressure techniques (sapphire anvil cells, SAC) and spectroscopic methods (Raman spectroscopy and FTIR) to demonstrate whether or not the pressure can be considered as an important geological agent in the formation of the resinites.

The obtained results show a general broadening in the spectral bands, in addition to a shift to higher wavenumbers with pressure, indicating that sample does not experience significant changes as confirmed by the observation of no colour change in the recovered sample.

According to the spectroscopic results, the *trans*-communic acid experiences slight conformational changes in the explored pressure range but no evidence of pressure-induced polymerization was observed, in contrast high-temperature treatments [7].

We can conclude that within the experimental conditions, pressure cannot be considered as an important geological agent in the formation process of the fossil resins.

Acknowledgments

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