SUPPLEMENTARY MATERIAL

Gallic acid as main product in the water extractives of *Quercus frainetto* Ten.

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The autoclave extraction of *Quercus frainetto* wood gave 5.3% extractives. The chloroform soluble fraction obtained from the extracts of *Q. frainetto* allows to identify sesamin. The insoluble fraction contains mainly ribose and mannose. Water extraction in autoclave of thermo-treated Q. frainetto wood gave a lower amount of extractives (3.31%). The main product of the insoluble fraction was, on the basis of its mass spectrum, the monoacetyl derivative of gallic acid.

Keywords: *Quercus frainetto*; thermo-treated wood; extractives.

3. Experimental

Sample preparation and heat treatment

This study used 40 free defect boards of *Q. frainetto*, which were collected in December 2015. Four trees with an average diameter of 60 cm from Vallone di Castagna of National Park Gallipoli Cognato (Basilicata Ragion, Italy, lat. 40°29'60 long. 16°05'40) were cut. Eight boards were then cut from these trees and thermally modified at a vacuum plant system, developed by WDE Maspell sl (Terni, Italy), located at the University of Basilicata.

A total of eight sawn boards randomly selected with dimensions of 30 mm × 150 mm × 1000 mm (thickness × width × length, respectively), having a moisture content of 20%, were used for the thermal treatment. Other eight boards were stored as reference (untreated).

Boards were thermally modified at a vacuum plant, developed by WDE Maspell srl (Terni, Italy), located at the University of Basilicata. A dual function machine was used, which can dry wood under vacuum conditions and treat wood at a high temperature (up to 250 °C). The laboratory kiln (4 × 1 m) can hold two layers of boards, which are loaded manually. Boards lie between two metal plates, which contain diathermic hot oil that provides conductive heat transfer to the boards. Pressure in the kiln can be regulated in the range 60–1000 mbar. Vacuum is maintained through a water ring-type pump equipped with a heat exchanger. Under pressure, the plates provide a force on the boards that prevents potential deformation of the wood (Ferrari et al., 2013).

The samples were dried to a moisture content of 0% in the same system prior to the thermo-vacuum treatments. The drying process of the samples having an initial moisture content of 20% was carried out at 100 °C and a pressure not exceeding 25,000 Pa, corresponding to a water boiling temperature of 65 °C.

In the next step, samples were exposed to the thermo-vacuum treatment. Each thermo-vacuum treatment consisted of a heating phase that started at a temperature of 100 °C and reached a maximum of air temperature of 190 °C followed by a thermal treatment phase with 200 °C air temperature for 2 h.

Three-hour cooling phase decreased the temperature of the samples to 100 °C. The heating rate of the air was 12 °C/h. The temperature variation of the diathermic oil, air, and wood samples was measured using thermocouples. Sixteen little specimens, 30 mm × 150 mm × 10 mm (thickness × width × length, respectively), equally distributed between thermo-treated and untreated boards, were then cut from the boards and reduced to a small size with a small rotary blade machine.

Randomly selected powder wood samples from untreated and wood heated at 200 °C were prepared and subjected to the chemical evaluations reported in the below sections. For the both extraction procedures (soxhlet and autocalve) and for other determinations each test was repeated three times.

Soxhlet Extraction

The samples of wood obtained in “Sample preparation and heat treatment” section were dried at 105°C overnight. Then, it was ground through a 40 mesh screen using a Wiley Mill.

The obtained material (1.0 g) was put into an extraction thimble, and it was put into a Soxhlet extraction apparatus. The sample was extracted with 300 ml of 1:2 ethanol/toluene mixture (v/v) for 7 h. After this period, the solvent was then evaporated in vacuo.

Lignin Content

The remaining sawdust was transferred to a 50-ml beaker, a cold H_2SO_4 solution (72%) (15 ml) was added, and the mixture was frequently stirred for 2 h at room temperature.

The mixture was then diluted to 3% (w/w) with 560 ml of distilled water, heated under reflux for 4 h, filtered, and washed with 500 ml of water. The residue was dried at 105 °C to a constant mass. The holocellulose content was determined by difference between the residue amount after extraction and the lignin content.

Autoclave Extraction

A sample of wood (10 g) was put into an airtight glass jar with 50 ml of distilled water and placed into the autoclave (Vapor Matic 770) for 20 min., at a temperature of 120 °C and a pressure of 1 bar for the extraction. Sample was filtered and frozen at a temperature of −28 °C. Then, it was lyophilized to remove water. The obtained mixture was fractionated as follows: the mixture was treated with chloroform (20 ml) and filtered, the solvent was evaporated, and the residue was chromatographed using tin layer chromatography on silica gel in the presence of a fluorescent indicator and using an hexane/ethyl acetate mixture. The different zones revealed by UV irradiation were separated and eluted with ethyl acetate. The solvent was evaporated, and the residue was analyzed as described in "Gas chromatographic–mass spectrometric analyses" section. The chloroform insoluble fraction was treated as described in "Derivatization" section.

Derivatization

To about 100 mg of the chloroform insoluble fraction of the extractives, 1 ml of pyridine and 1 ml of acetic anhydride were added, and the sample was allowed to sit at room temperature for 48 h. Then, the solvent was exchanged with ethanol under reduced pressure followed by drying in vacuo. The residue was chromatographed using tin layer chromatography on silica gel in the presence of a fluorescent indicator. The different zones revealed by UV irradiation were separated and eluted with ethyl acetate. The solvent was evaporated, and the residue was analyzed as described in "Gas chromatographic-mass spectrometric analyses" section.

Gas Chromatographic-Mass Spectrometric Analyses

Analyses of all the extractives obtained using all the procedures previously described were accomplished with an HP 6890 Plus gas chromatography equipped with a Phenomenex Zebron ZB-5 MS capillary column (30-m × 0.25-mm i.d. × 0.25 μm FT) (Agilent, Milan, Italy). An HP 5973 mass selective detector (Agilent) was utilized with helium at 0.8 ml/minas the carrier gas. A

split injector was maintained at 250°C, and the detector at 230 °C. The oven was held at 80 °C for 2 min, then gradually warmed, 8°C/min, up to 250 °C and held for 10 min. Tentative identification of aroma components was based on mass spectra and NIST11 library comparison.

Table S1. GC-MS analysis of chloroform soluble water extractives

Compound	r.t. [min]	Area [%]
Benzaldehyde	4.31	0.02
Pentanoic acid	4.36	0.02
Limonene	5.12	0.02
Phenol	5.45	0.02
2-Furancarboxylic acid	5.54	0.09
Maltol	6.06	0.04
5-Hydroxymethyl-furfural	7.15	0.19
Benzeneacetic acid	7.30	0.04
Nonanoic acid	7.40	0.06
2-Methoxy-4-vinylphenol	7.89	0.05
trans-3-Methyl-4-octanolide	7.96	0.04
2,6-Dimethylphenol	8.16	0.39
Eugenol	8.21	0.07
Vanillin	8.54	0.38
(2-Methoxyphenoxy)-acetic acid	8.83	0.05
trans-Isoeugenol	8.88	0.05
3,4,5-trimethoxyphenol	9.85	0.16
4-Hydroxy-3,5-dimethoxybenzalde-hyde	10.23	1.49
4-Hydroxy-3,5-dimethoxybenzoic acid	11.07	0.75
Methyl 3,4-dimethoxymandelate	11.92	0.58
3,5-Dimethoxy-4-hydroxycinnamaldehyde	11.99	0.69
Octadecanoic acid	12.92	0.20
Octadecane	16.18	0.07
Sesamin	17.22	4.68
Eicosane	19.79	0.19
Methyl 3-(1-formyl-3,4-methylenedioxy)-benzoate	23.92	0.65
(1-Ethyl-2-benzimidazolyl)(1-naphthyl)methanol	26.73	10.12
β-Sitosterol	30.73	0.16

Table S2. GC-MS analysis of chloroform insoluble water extractives after acetylation.

Compound	r.t. [min]	Area [%]
Furfural	3.25	0.26
β-D-ribonopyranose tetraacetate	10.93	2.78
1,2,3,5-Tetra-O-acetyl-β-D-ribofuranose	11.01	3.26
Lyxopyranose tetraacetate	11.14	8.60
Iditol hexaacetate	11.34	1.33
β-D-Galactopyranose pentaacetate	12.40	2.42
α-D-Glucopyranose pentaacetate	12.45	1.96
D-Galactofuranose pentaacetate	12.77	2.45
Muco-inositol hexaacetate	12.90	3.35
Meso-gluco-gulo-heptitol heptaacetate	13.08	1.06

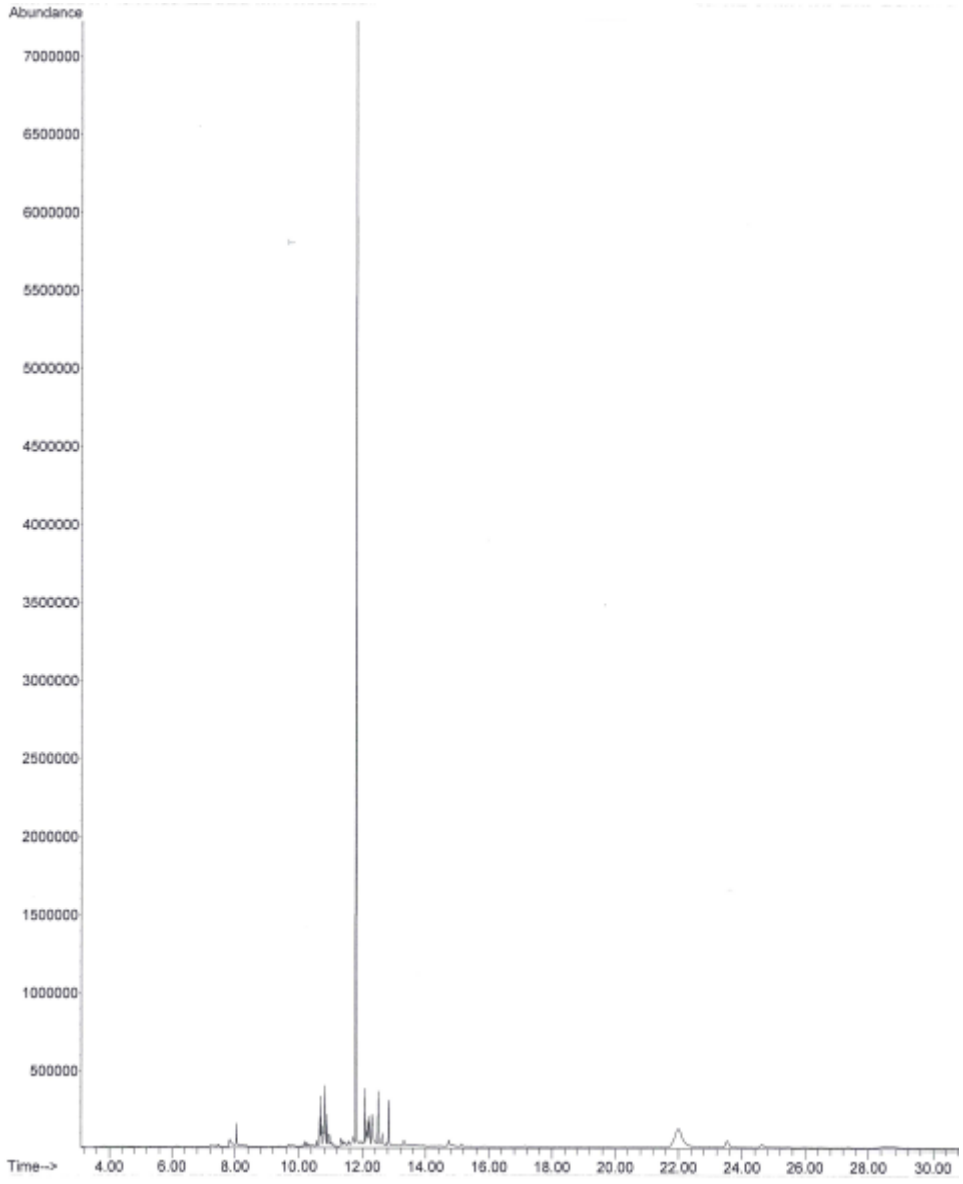

Figure S1. Chromatogram of the chloroform insoluble fraction of water extractives of thermo-treated *Q. frainetto* wood.

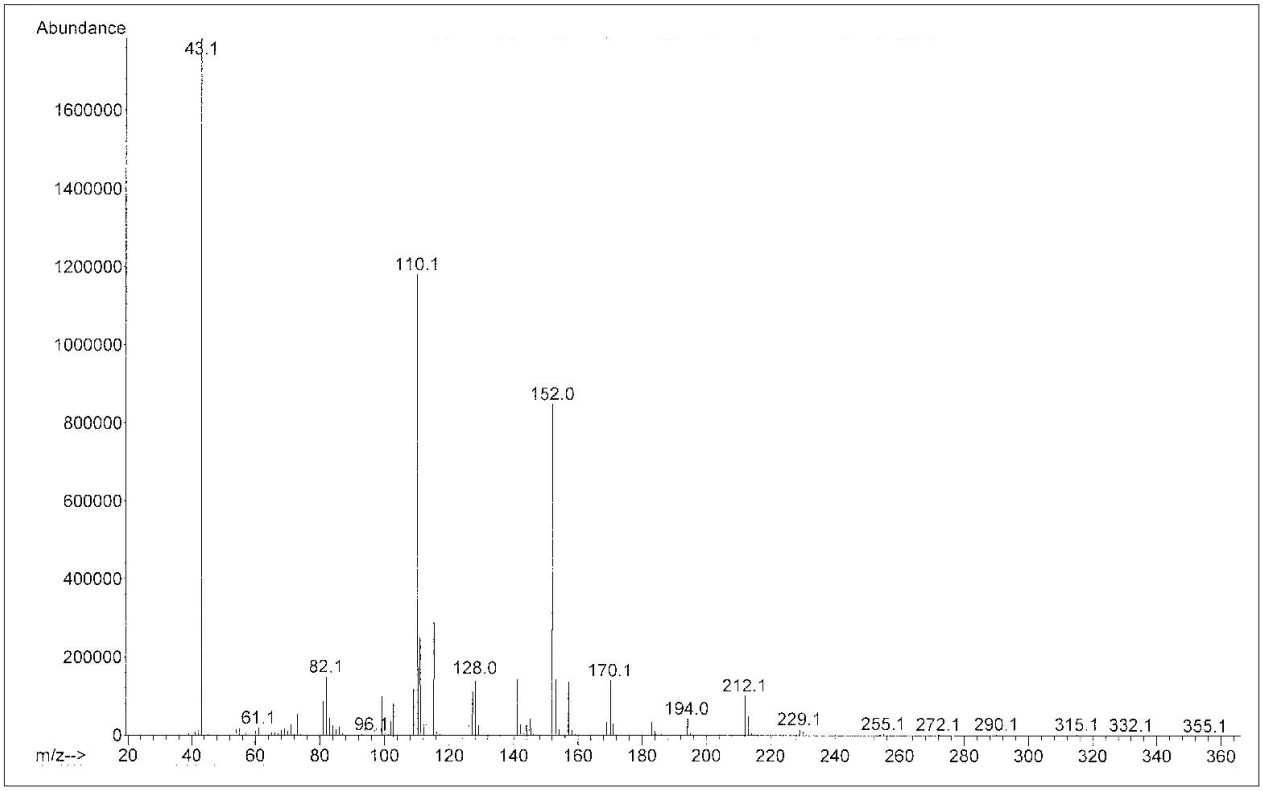

Figure S2. Mass spectrum of the main product present in the extracts of thermo-treated *Q. frainetto* wood.