

Analysis of Valonia Oak (*Quercus aegylops*) Acorn Tannin and Wood Adhesives Application

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The coupling of matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectrometry with ¹³C nuclear magnetic resonance (NMR) is a suitable method for examining the composition of hydrolysable tannins and has been applied to the investigation of valonia oak (*Quercus aegylops*) acorn tannin extract. Such methods can determine the extract's structural aspects and other characteristics. It was determined that valonia oak acorn tannin extract is composed of mainly pentagalloylglucose structures; their rearrangement structures, vescalagin/castalagin (with linkages to flavogallonic acid) and vescalin/castalin; ellagic acid and vescaloneic/castavaloneic acid; and free gallic acid and glucose. Traces of catechin gallate were also observed in this tannin extract. The tannin from acorns of valonia oak was used to substitute up to 50% of the phenol used in the preparation of phenolic resins as adhesives for wood particleboard. These phenol-tannin-formaldehyde resins showed comparable performance to phenol-formaldehyde resins.

Keywords: MALDI; Mass spectrometry; ¹³C NMR; Hydrolysable tannins; Structure; Structural composition; Oligomer distribution; Wood panels; Phenolic adhesives

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INTRODUCTION

Hydrolysable and condensed tannins are natural materials that are receiving increasing attention due to the development of alternative, environmentally-friendly applications outside their traditional use in leather tanning (Pizzi 1994). The relatively limited quantities of the traditional, commercial tannins available today in the world market that can be spared for uses besides leather tanning have created demand for the exploration of other available tannin-producing species. Valonia oaks (*Quercus aegylops*) are a species now widely cultivated in the Mediterranean basin, and their acorn tannins can be used industrially for leather manufacturing. Their availability renders them an interesting source of natural, biosourced, and environmentally-friendly materials for the preparation of resins for different applications. They are mainly hydrolysable-type tannins, which have been researched much less than their condensed counterparts for resin applications (Pizzi 1994; Pizzi and Meikleham 1994; Tondi *et al.* 2008, 2009a,b; Tondi and Pizzi 2009; Abdullah *et al.* 2013, 2014; Lagel *et al.* 2014a, 2015). However, suitable technologies for their use in resins, such as wood adhesives and rigid foams, have recently emerged for commercial chestnut wood tannin extract, another hydrolysable tannin (Spina *et al.* 2013; Lagel *et al.* 2014b,c). Thus, hydrolysable tannins, as equally diffuse in nature as condensed tannins,

constitute an interesting and largely unexploited reserve of natural renewable materials for the preparation of resins.

The structures and distribution of the main monomers and oligomers constituting valonia oak acorn tannin have been scantily explored. As different hydrolysable tannins present different structures, molecular mass distributions, and degrees of polymerisation (Pasch and Pizzi 2002; Pizzi *et al.* 2009; Giovando *et al.* 2013; Radebe *et al.* 2013), it is necessary to define their characteristics to understand what type of resin technology could be used for their industrial exploitation. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry has greatly expanded the use of mass spectrometry in characterizing large molecules and has also revealed itself to be a powerful method for the characterization of different oligomers in polyflavonoid tannins (Pasch *et al.* 2001; Oo *et al.* 2008; Navarrete *et al.* 2010). MALDI and ^{13}C nuclear magnetic resonance (NMR), a technique indispensable in the chemical definition of these materials, constitute a powerful set of techniques to determine their constituent structures and advance the production of resins for different applications. In this research, the application of valonia oak tannin extract as a substitute for phenol in phenol-formaldehyde resins for wood adhesives is reported.

EXPERIMENTAL

Materials

Acorns from valonia oaks were imported from Turkey. The acorns were dried in the open air, then reduced to a fine powder with a particle size of about 50 μm using a Retsch SK1 (Germany) knife mill.

Extraction of Tannins

The extraction of the tannin was carried out using 900 g of acorn powder. The extraction was performed three times by placing 300 g of fine acorn powder into a beaker, and deionized water was added at a 1:5 proportion of acorn powder to water. The temperature was maintained at 70 °C for 6 h with continuous, vigorous mechanical stirring of the suspension of powder in water. The extract yield was about 15% based on the dry powder. After filtration, washing with water, and pressing of the dried residue, the three solutions were combined. Using a rotary evaporator, under vacuum, at 40 °C, the volume of the solution was decreased to one-third of its original value. The solution was then spray-dried with a laboratory spray drier (BUCHI mini spray dryer B-290, Switzerland). The spray drying was performed with an inlet temperature of 150 °C, an aspirator output of 100% and a pump rate of 10%.

MALDI-TOF Analysis

Operating conditions

The spectra were recorded on a Kratos MALDI Axima TOF 2 instrument (Kratos Analytical, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm, and the length of one laser pulse was 3 nsec. The measurements were carried out using conditions of positive polarity, a linear flight path, and high mass (20 kV acceleration voltage), with 100 to 150 pulses per spectrum. The delayed extraction technique was used, applying delay times of 200 to 800 nsec.

MALDI-TOF sample preparation

The samples were dissolved in acetone (4 mg/mL, 50:50% by volume). The sample solutions were then mixed with an acetone solution (10 mg/mL in acetone) of 2,5-dihydroxybenzoic acid as a matrix. For the enhancement of ion formation, NaCl was added to the matrix (10 mg/mL in water). The solutions were mixed in proportions of 3 parts matrix solution to 3 parts tannin extract solution to 1 part NaCl solution, and 0.5 to 1 μ L of the resulting solution mix was placed on the MALDI target. After the evaporation of the solvent, the MALDI target was introduced into the spectrometer. A value of 23 Da must be subtracted from each peak value in the resulting positive mode spectrum to account for the Na⁺ ion of the matrix and to obtain the molecular weight of the chemical species of the peak.

¹³C NMR Analysis

The sample was prepared by diluting a 40% by mass aqueous solution of spray-dried *Quercus aegylops* tannin extract powder with D₂O in a 1:4 mass proportion. The ¹³C NMR spectra were obtained on a Bruker AC200 FT-NMR spectrometer (France) at a frequency of 50.3 MHz, with the sample spectra set at 25 Hz. Chemical shifts were calculated using (CH₃)₃Si(CH₂)₃SO₃Na as an NMR control. (CH₃)₃Si(CH₂)₃SO₃Na was dissolved in D₂O and run separately, and the shifts for the four signals were set. All spectra were run overnight. The acquisition time was 1.08 s and the number of transients was approximately 10,000. The spectra were run with a relaxation delay of 5 s and an accuracy of 1 ppm. The spectral width was 15,000 Hz, with a digital resolution of 0.925 Hz per point with exponential multiplication. Typical spin lattice relaxation times were not measured, but standard values shown in the literature were used (Breitmaier and Voelter 1987).

Wood Panel Adhesive PF Tannin Resin Preparation

Spray-dried acorn tannin extract powder obtained from valonia oaks was used for this purpose. The resin, based on a phenol-formaldehyde-tannin extract, was prepared using a PF to tannin extract mass proportion of 48:52, corresponding to a resin with an effective phenol content of 46.7% and tannin extract solids of 53.3%.

Samples of 85 g of valonia oak acorn tannin extract and 85 g of 90% phenol were dissolved in a water-methanol solution (62.7 g water, 9.6 g methanol), to which 95.5 g of 96% paraformaldehyde powder (Degussa N, Germany) was added, premixed with 4 g of water. The reaction mixture was maintained at 40 °C for 30 min, under continuous mechanical stirring, in a glass reactor equipped with a reflux condenser. The mixture was then heated until the temperature reached 94 °C, and 45.2 g of 30% aqueous NaOH solution was added in 4 equal lots at 15-min intervals. After the addition of the last lot of NaOH solution (45 min from the start of the NaOH addition period), the reaction mixture was heated for an additional 15 min, to reach a total of 1 h of reaction time, then cooled and stored. The resin obtained had a viscosity at 25 °C of 550 to 600 cP, a solids content of 61% and a pH of 8.6, which was then adjusted to a pH of 11 by the addition of 18.4 g of a 30% NaOH aqueous solution. This pH adjustment caused a decrease in the solids content and viscosity to 55.8% and 375 to 400 cP, respectively. The PF resin control was prepared according to the same procedure of the PTF resin by substituting the 85 g of valonia tannin extract with 75 g of 90% phenol, the rest of the procedure being the same.

Wood Particleboard Preparation and Testing

One-layer laboratory particleboards with dimensions of 350 mm × 300 mm × 14 mm were prepared by mixing core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) at a maximum pressure of 28 kg/cm² and a press temperature of 195 °C. The resin solids content was maintained at 10% of the total mix. The total pressing time was 7.5 minutes. All particleboards were tested for internal bond (IB) strength on an Instron 3369 test machine (High Wycombe, UK). The 48:52 PF-valonia oak tannin adhesive was used to prepare 10 laboratory panels. For accelerated aging tests, specimens were boiled in water for 2 h, dried at 103 °C for 16 hours, and tested for residual IB strength using an Instron 3369 test machine (UK).

RESULTS AND DISCUSSION

The interpretation of the MALDI-TOF spectra shown in Figs. 1a and 1b yielded the series of structures listed in Table 1. The spectra peak values are the sum of the 23 Da, belonging to the Na⁺ ion used to enhance the spectra, and of the molecular weight of the species. The results confirmed that valonia oak acorn tannins are mainly hydrolysable tannins, with only some traces (1% or lower) of flavonoids present. The only peak belonging to a flavonoid was at 441 Da, characteristic of the catechin monogallate monomer; there were no others evident in the spectra. In monomeric flavonoids it is often being observed that the peaks are not with Na⁺, thus they directly reflect the M.W. of the monoflavonoid. The equivalent compound with Na⁺ can either be observed or frequently not observed. Many examples of this effect have already been observed (Ucar *et al.* 2013; Abdalla *et al.* 2014; Thebault *et al.* 2015; Drovou *et al.* 2015; Li *et al.* 2015).

Peaks at 193 Da and 203 Da belonging to gallic acid and glucose, respectively, were also present.

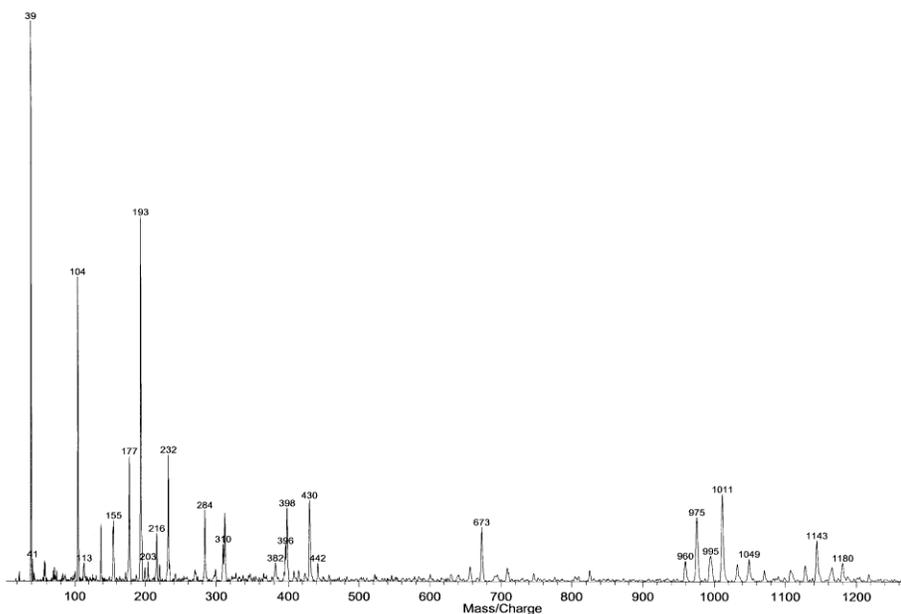


Fig. 1a. MALDI-TOF spectra of valonia oak acorn tannin in the 25 to 1400 Da range

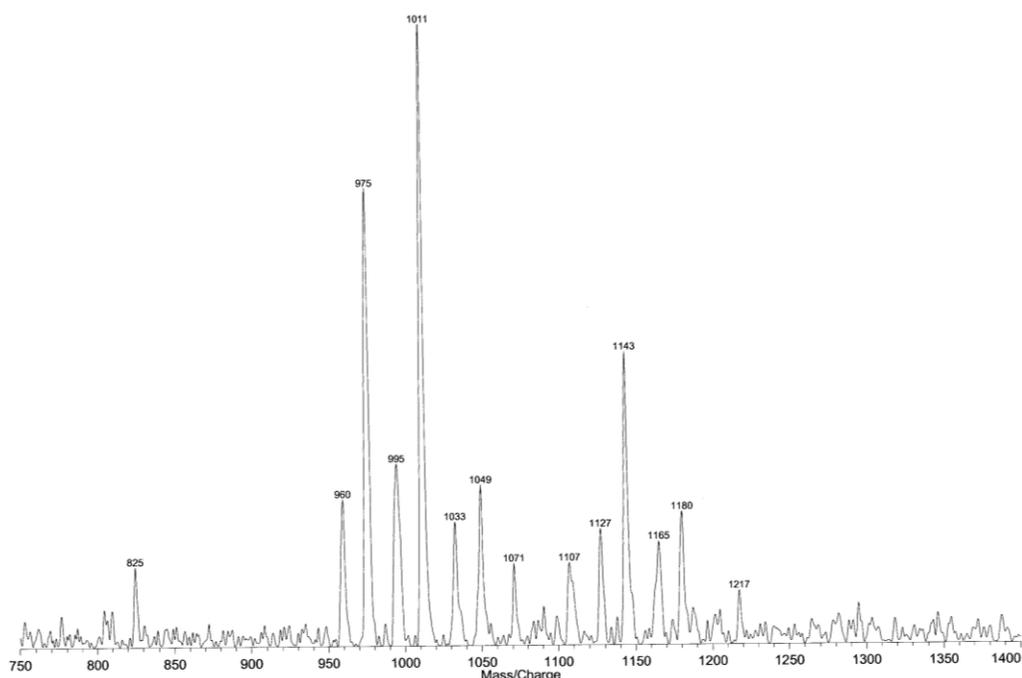


Fig. 1b. MALDI-TOF spectra of valonia oak acorn tannin in the 750 to 1400 Da range

The relative percentage of condensed tannins was very small, around 1% as shown by the only catechin gallate peak in the MALDI-TOF spectra. In regards to the total polyphenolic materials this is in excess of 87% if one considers the carbohydrate residues attached to pentagalloylglucose, vescalin, and vescalagin species as inherent part of the polyphenolic tannin.

Shifts of 471 Da, such as those between the 655-Da and 1127-Da peaks and between the 673-Da and the 1143-Da peaks, were also evident (Figs. 1a and 1b), corresponding to a flavogallonic acid structure (Fig. 2), thus a 486 Da MW of a diprotonated flavogallonic acid minus a $-OH$ group where it is linked to the castelin/vescalin structure. Structures formed by two flavogallonic acid structures linked to a single glucose were also present, as shown by peaks at 1011 Da.

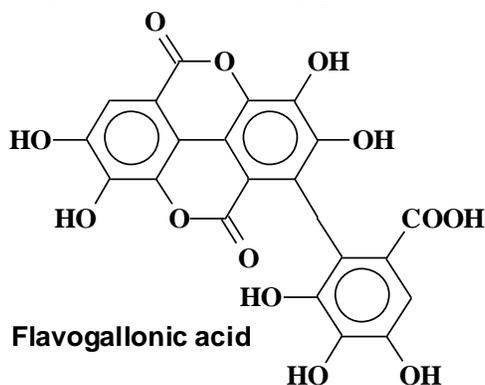


Fig. 2. Structure of flavogallonic acid

Shifts of 302 Da, indicating the presence of ellagic acid structures, such as those between the 673-Da and 975-Da peaks, were also apparent (Fig. 1b). Galloyl residues of 152 Da, such as between the 1143-Da and 975-Da peaks, were also apparent in the spectra (Fig. 1b). The main structures occurring in hydrolysable tannins are two types of structures formed from the degradation and rearrangement of pentagalloylglucose: vescalagin/castalagin (I) at 960 Da and vescalin/castalin (II) at 655 Da (Fig. 3).

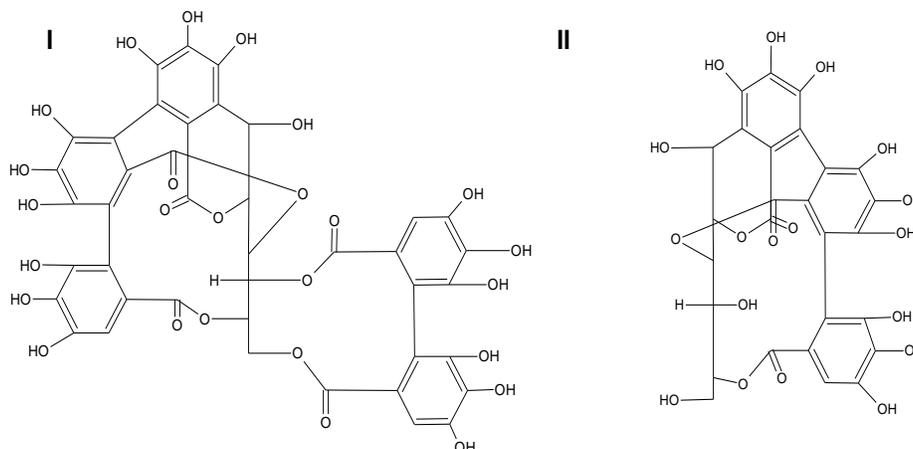


Fig. 3. Structures of vescalagin/castalagin (I) and vescalin/castalin (II)

The peak at 960 Da could either belong to vescalagin/castalagin (I) (Fig. 3) or to pentagalloylglucose (Fig. 4), the former being a rearrangement of the latter with a very similar molecular weight.

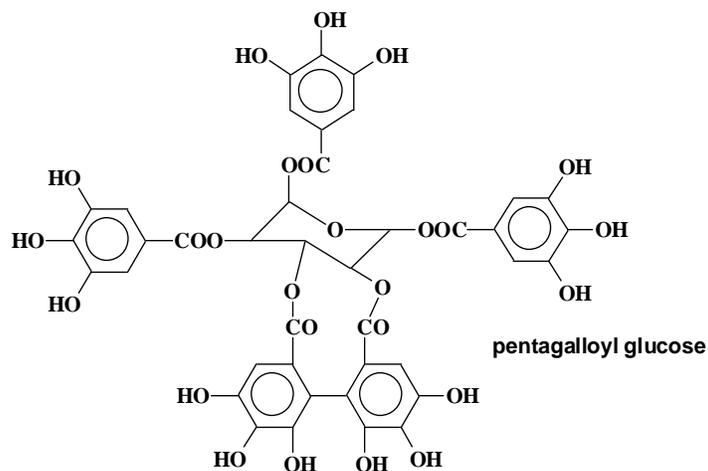


Fig. 4. Structure of pentagalloylglucose

The peak at 1127 Da belonged to the vescavaloneic/castavaloneic acid structure (Fig. 5).

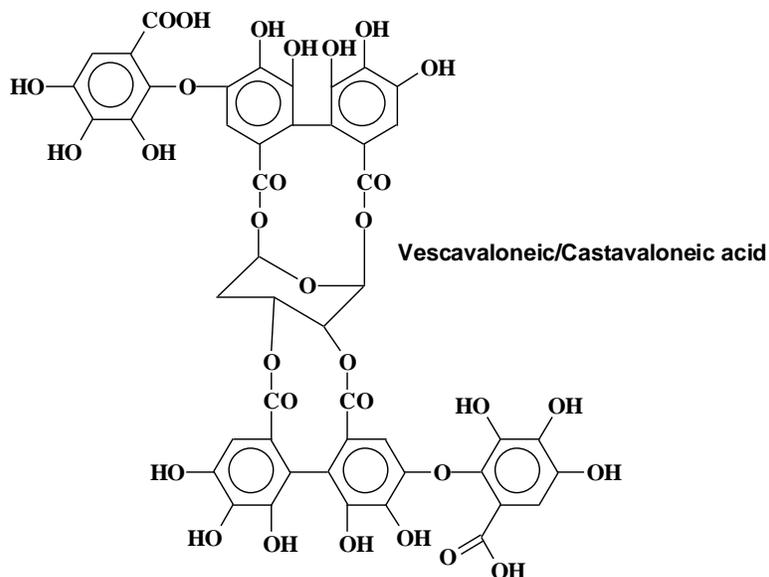


Fig. 5. Structure of vescavaloneic/castavaloneic acid

Table 1. Results of MALDI-TOF Spectra of the Tannin Extracted from the Acorns of Valonia Oak, with Na⁺ Enhancement

Experimental Mass (Da)	Calculated Mass (Da)	Oligomer Type
193	193	Gallic Acid
203	203	Glucose
442	442	Catechin Monogallate Monomer
655	655	Castalin/Vescalin
673	672	Castalin/Vescalin +1 × (-OH)
825	702	Castalin/Vescalin +1 Galloyl Residue +1 × (-OH)
960	957	Castalagin/Vescalagin
960	963	Pentagalloyl Glucose
975	1099	Castalagin/Vescalagin +1 × (-OH)
1107	1107	Castalagin/Vescalagin +1 Galloyl Residue
1011	1012	1 Glucose Linked to Two Flavogallonic Acid Residues
1127	1127	Vescavaloneic/Castavaloneic Acid OR Castalin/Vescalin +1 × Flavogallonic Acid Residue OR Pentagalloylglucose +1 × Galloyl Residue
1143	1143	Castalin/Vescalin +1 × Flavogallonic Acid Residue + 1 × (-OH) OR Vescavaloneic/Castavaloneic Acid + 1 × (-OH)

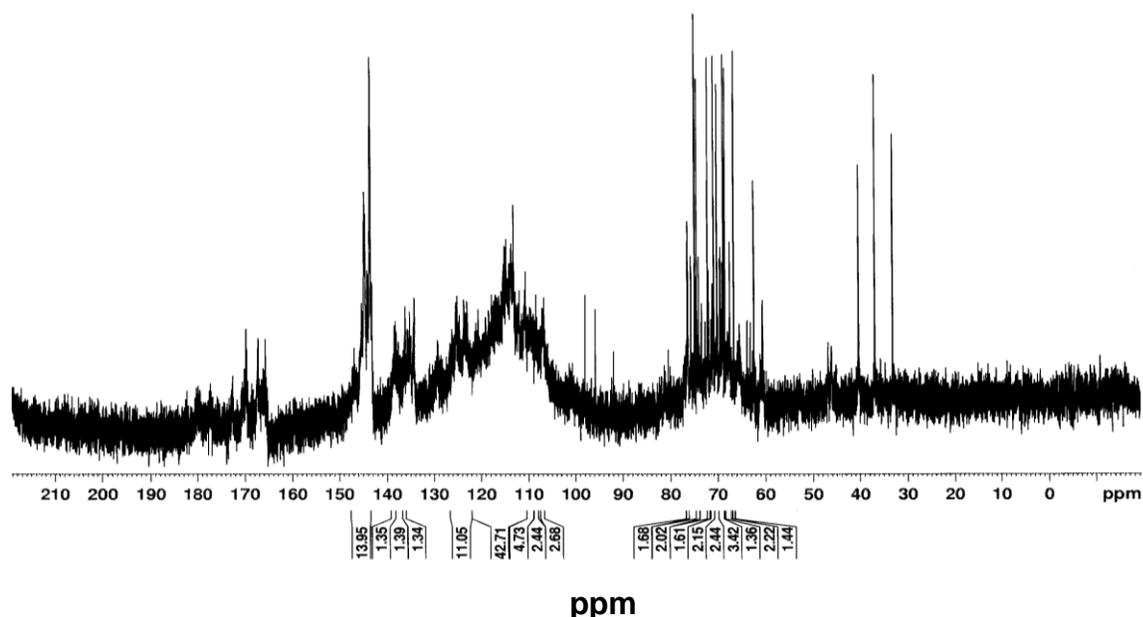


Fig. 6. ^{13}C NMR of valonia oak acorn tannin

The ^{13}C NMR spectrum (Fig. 6) shows the shifts belonging to pentagalloyl glucose (Fig. 4) and to vescalagin/catalagin (Fig. 3), occurring at 62.9, 67.1, 68.8, 70.0, 70.3, 122.7, 137.8, 164.7, and 166.7 ppm; these two latter values belong to the $-\text{COO}-$ ester groups present in these compounds. In the glucose range, between 60 and 80 ppm, shifts were noticed at 68.1 and 72.9 ppm, which were characteristic of the open glucose forms of vescalagin/castalagin and vescalin/castalin, respectively, while the 90.4-ppm shift was characteristic of the closed glucose form (Pasch *et al.* 2001; Pasch and Pizzi 2002; Pizzi *et al.* 2009; Radebe *et al.* 2013). The 106.5- and 109.5-ppm shifts characteristic of vescalagin/castalagin were also observed in the spectrum depicted in Fig. 6. The carboxyl group of the gallic acid was observed at 168.2 ppm. The other shifts of gallic acid were observed at 138.9 ppm (C1 bonded to an $-\text{OH}$ group), 145.3 ppm (C2, C6), 125.1 (C4 bonded to the $-\text{COOH}$ group), and 117.5 ppm (C3, C5). These results confirm that the tannin extract from the acorns of valonia oak is predominantly a hydrolysable tannin, mainly composed of pentagalloylglucose and its rearrangement compounds, vescalagin/castalagin and vescalin/castalin. Free glucose and gallic acid were present as flavogallonic acid, ellagic acid, and vecavaloneic/castavaloneic acid.

Confirmation of coreaction of tannin and phenol is obtained by the MALDI-TOF spectrum of the PTF resin. MALDI-TOF analysis can be performed in either positive or negative ion modes (Pasch *et al.* 2002). In the case of hydrolysable tannins the positive mode spectrum shows what happens to the phenolic component of the material while negative ion mode analysis shows what happens to the polymeric carbohydrates of the system (Pasch *et al.* 2002). Positive mode MALDI-TOF analysis is commonly performed,

while negative mode is used rarely. Thus, Fig. 7 and Table 2 show the oligomers that are formed from the phenolic component of the phenol-tannin-formaldehyde resin during the preparation and of the resin (the sample was not cured but just air dried).

Table 2. MALDI-TOF Spectrometry Peaks, Corresponding Oligomers Formed, and the Relative Peak Intensity Percentages for a PF/Valonia Oak Acorn Tannin 50/50 Co-reacted Resin

M+Na ⁺ (Experimental) (Da)	M+Na ⁺ (Calculated) (Da)	Relative peak intensity (%)	Oligomer type *
233.9	236	3.5	PCH ₂ PCH ₂ ⁺
263.7	264	7.1	HOCH ₂ PCH ₂ PCH ₂ ⁺
277.8	277	0.7	HOCH ₂ PCH ₂ P(CH ₂ ⁺) ₂
299	299	3.8	G CH ₂ P
312.5	312	4.7	G CH ₂ PCH ₂ ⁺
327	328	3.5	G CH ₂ PCH ₂ OH or G CH ₂ OCH ₂ P
343.7	343	9.9	PCH ₂ PCH ₂ PCH ₂ ⁺
358.4	359	2.8	PCH ₂ PCH ₂ PCH ₂ OH
373.5	373.7	9.8	HOCH ₂ PCH ₂ PCH ₂ PCH ₂ ⁺
375	375	2.7	G CH ₂ G
386.5	387	3.6	HOCH ₂ PCH ₂ PCH ₂ P(CH ₂ ⁺) ₂
403	403	4.7	(HOCH ₂) ₂ PCH ₂ PCH ₂ PCH ₂ ⁺ or G CH ₂ OCH ₂ G
408	406	4.8	G CH ₂ PCH ₂ P
419.6	419	0.4	(HOCH ₂) ₂ PCH ₂ PCH ₂ PCH ₂ OH
430.9	432	4.4	(HOCH ₂) ₂ PCH ₂ P(CH ₂ ⁺)CH ₂ PCH ₂ OH
449.9	450	1.5	(HOCH ₂) ₂ PCH ₂ PCH ₂ P(CH ₂ OH) ₂
480.1	481	9.6	G CH ₂ PCH ₂ G
493.4	494	1.8	G CH ₂ PCH ₂ G CH ₂ ⁺
510.3	511	3.0	G CH ₂ PCH ₂ G CH ₂ OH
553	553	1.2	HOCH ₂ G CH ₂ P(-CH ₂ ⁺)CH ₂ G CH ₂ OH
566.4	568	1.0	HOCH ₂ G CH ₂ P(CH ₂ OH)CH ₂ G CH ₂ OH
577.6	578	2.0	HOCH ₂ G (CH ₂ ⁺)CH ₂ P(CH ₂ OH)CH ₂ G CH ₂ OH
599.1	599	2.0	G CH ₂ PCH ₂ G CH ₂ PCH ₂ ⁺
607.2	608	4.2	(HOCH ₂) ₂ PCH ₂ P(-CH ₂ G)CH ₂ PCH ₂ OH or (HOCH ₂) ₂ PCH ₂ P(-CH ₂ OCH ₂ G)CH ₂ P
752.6	752	1.6	oligomer at 769 Da-1x-OH group
769	770	0.8	G CH ₂ PCH ₂ G CH ₂ PCH ₂ G
782.8	782	0.9	G CH ₂ PCH ₂ G CH ₂ PCH ₂ G CH ₂ ⁺
798	799	0.5	G CH ₂ PCH ₂ G CH ₂ PCH ₂ G CH ₂ OH
815.3	816	0.8	HOCH ₂ G CH ₂ PCH ₂ G CH ₂ PCH ₂ G CH ₂ ⁺
888.9	888.8	0.5	G CH ₂ PCH ₂ G CH ₂ PCH ₂ G CH ₂ PCH ₂ ⁺

* G are the peaks where the tannin is present. P are the peaks where phenol is present.

A number of co-reacted phenol-tannin oligomers are formed, confirming the NMR result. The tannin contribution is indicated as "G" (for "gallic acid), this being calculated as gallic acid equivalents (Table 2). Thus, definitely belonging to co-reacted mixed species are the series of peaks at 299, 312, 403, 480, 493, 510, 553, 566, 577, 599, 607, 769, 782, 799, and 888 Da, constituting 66% of the total number of species of the polymer and 50% of the total mass of the polymer. Mixed species may also contribute to the peaks at 327 Da

and 403 Da. The rest of the peaks belong to pure phenol-formaldehyde (PF) oligomers. This also confirms that a species such as gallic acid, which has both sterically hindered sites and those in *meta* position to some of the phenolic –OH groups, is rather reactive and forms through these *meta* sites methylene bridges with the *ortho* and *para* sites of the synthetic phenol.

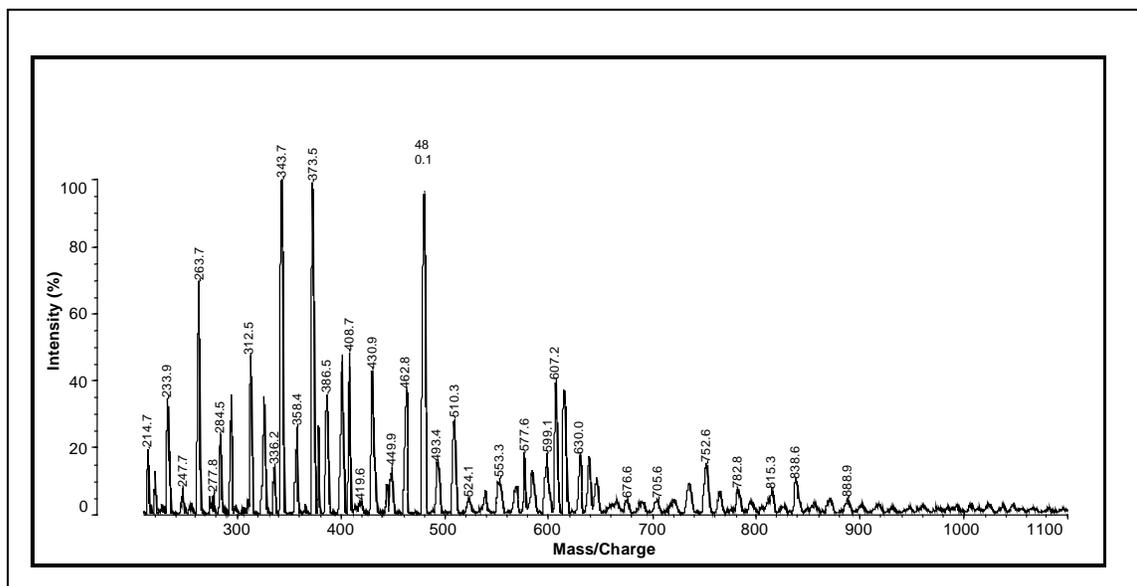


Fig. 7. MALDI-TOF spectrum of air-dried coreacted 50/50 PF/chestnut tannin adhesive

The tannin extract of valonia oak acorns was tested for use in wood particleboard panels according to the technology developed by Spina *et al.* (2013) for chestnut tannins.

Table 3 reports the results of testing wood particleboard bonded with a phenol-tannin-formaldehyde resin obtained by the co-reaction of phenol and tannin with formaldehyde, producing a proportion of 50 parts raw tannin extract to 50 parts raw phenol by weight. The purity of the phenol used was 90%, and the spray-dried tannin moisture content was 4%; thus, the relative proportion by weight of phenol to tannin extract was 48:52.

To evaluate the effectiveness of bonding of a particleboard adhesive, the Internal Bond strength is the only test necessary, as the other mechanical properties of the final panel depends mainly on the panel density and the geometry of the wood particles used, and are not a real reflection of how good or bad the adhesive is.

The results in Table 3 indicated that at least 50% of the phenol could be effectively substituted by valonia oak acorn tannin and that a PTF resin could be prepared and used as a classical PF resin. The IB strength results of PF-bonded and PTF-bonded particleboard were comparable, with no significant differences. The 50:50 (48:52) proportion between phenol and a hydrolysable tannin was chosen based on previous work on chestnut tannin, which is also a hydrolysable tannin.

Table 3. Average Board Density and IB Strength for a Series of 10 Wood Particleboard Panels Prepared with 10% Solid Resin Content of a 48:52 PF-Valonia Oak Tannin Extract Adhesive

	Average board density (kg/m ³)	Average IB strength (MPa)	Formaldehyde Emission (mg/100g panel)
Experimental PTF ¹ boards	690	0.75	1.8
	692	0.72	1.8
	683	0.68	1.8
	703	0.72	1.9
	671	0.55	1.5
	686	0.62	1.3
	695	0.67	1.6
	701	0.70	1.8
	682	0.63	1.6
Average	687	0.66	1.7
PF ² control	694	0.62	1.8
EN 312:2010 requirement	-	>0.35	>6.5

¹Phenol-tannin-formaldehyde; ²Phenol-formaldehyde

CONCLUSIONS

1. The acorns of valonia oak were rich in hydrolysable tannins.
2. The MALDI-TOF and ¹³C NMR analyses allowed the identification of the structural units involved
3. The structures in this tannin were pentagalloylglucose, vescalagin/castalagin (with linkages to flavogallonic acid), vescalin/castalin with ellagic acid, vescavaloneic/castavaloneic acid, and free gallic acid and glucose also present.
4. Valonia oak acorn tannin is able to substitute at least 50% of the phenol used in the preparation of phenolic resin adhesives for wood particleboard with comparable results.

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