Matrix-Assisted Laser Desorption-Ionization Time of Flight (MALDI-TOF) Mass Spectrometry of Phenol-Formaldehyde-Chestnut Tannin Resins

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ABSTRACT: Natural hydrolysable chestnut tannin extracts used to partially substitute phenol in Phenol-Formaldehyde (PF) resins for phenolic rigid foams were analysed by matrix-assisted desorption ionization time of flight (MALDI-TOF) mass spectrometry. PF only, chestnut only and PF-chestnut copolymerised oligomer types and distribution were determined. MALDI-TOF analyses of a PF control resin (with the same molar ratio) and of chestnut tannin extracts were performed in order to identify the peaks of molecular weights corresponding to copolymers of chestnut tannins with phenol and formaldehyde.

KEYWORDS: Chestnut tannins, phenol-formaldehyde-chestnut tannins copolymers, MALDI-TOF analysis

1 INTRODUCTION

During the last decades a marked increase in oil prices has occurred. Consequently, considerable research has been carried out on the use of natural resources to replace petrochemicals. These developments have occurred in several diverse industrial sectors. Some research has concentrated on natural materials such as condensed polyflavonoid tannins to develop new biobased materials such as, for example, insulation foams or floral foams, biocomposites or biobased adhesive [1–6].

Most commercial tannins are industrially extracted by a simple water extraction from wood, bark, gall and other vegetable material. Two broad classes of tannins exist: in the first are the condensed polyflavonoid tannins. These have been extensively researched for adaptation to wood adhesives [5, 7], for fire-resistant tannin/furanic foams [8], and products/processes other than their traditional application for leather tanning.

The second class of tannins, namely hydrolysable tannins, are composed of polyphenolic oligomers of pentagalloyl glucose, and their lower reactivity has somewhat limited them to leather tanning, an application for which they are particularly prized due to their light color. Recently these tannins have been used to prepare phenol-hydrolysable-tannin-formaldehyde copolymer resins. These have been used for the preparation of phenolic wood adhesives [9, 10], and more recently for rigid fire-resistant foams [11].

There are two types of hydrolysable tannins such as chestnut, tara, turkey gall, oak, etc. The first type is composed of a mixture of sugars with oligomers of simple phenols such as gallic and digallic acids [12, 13], and the second type is composed of ellagitannins, which are esters of a sugar, mainly glucose, with gallic and digallic acids, and also with more complex structures containing ellagic acid (Formula 1).

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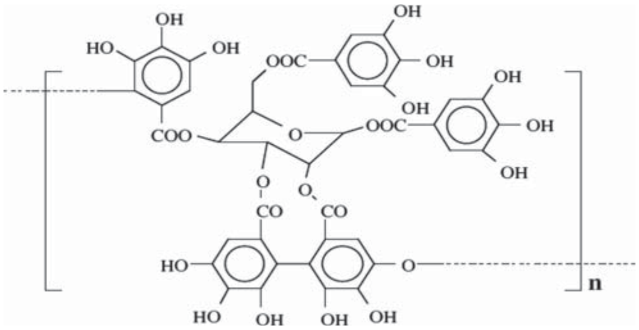


Formula 1

Chestnut wood tannin extract was the tannin chosen for this research being that it is the most abundant hydrolysable tannin [14]. The study presented here concentrates on the determination of the type and distribution of the oligomers formed in the reaction of phenol and chestnut tannin with formaldehyde to obtain phenol-hydrolysable-tannin-formaldehyde copolymer resins due to the results in fire-resistant phenol-formaldehyde-tannin foams recently developed [11]. This was done for continuity of the characterization of the resin developed in a previous work [9] to prepare rigid foams [11].

Since its introduction by Karas and Hillenkamp in 1987 [15], Matrix-Assisted Laser Desorption/Ionization (MALDI) mass spectrometry has greatly expanded the use of mass spectrometry towards large molecules, and has revealed itself to be a powerful method for the characterization of both synthetic and natural polymers [16–21]. Fragmentation of analyte molecules upon laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result, intact analyte molecules are desorbed and ionized along with the matrix and can be analysed in a mass spectrometer. This soft ionization technique is mostly combined with time-of-flight (TOF) mass analysers. This is because TOF-MS has the advantage of being capable of providing a complete mass spectrum per event for virtually an unlimited mass range, with only a small amount of analyte being necessary and relatively low cost of equipment. Its usefulness in the elucidation of the distribution of different oligomers in the case of polyflavonoid tannins in general has already been demonstrated [21–26]. In particular, its applicability for the identification of the oligomers distribution of hydrolysable tannins has also been demonstrated [14, 27, 28].

Thus, MALDI-TOF mass spectrometry has been used for this study, as it has already proven itself in the analysis of different types of tannins [12–14, 27, 29, 30]. For this study, three investigations were carried out: (1) for chestnut tannin extract alone, (2) for PF resin alone, and (3) for PF-chestnut tannin resin. In this article the characteristics of just the raw chestnut tannin extract and the PF resin by itself are only briefly discussed to help the reader compare these with what was obtained for the PF-tannin copolymer. For a more comprehensive discussion of the oligomers distribution obtained by MALDI-TOF mass spectrometry for raw chestnut tannin extract and for the PF resin alone, the reader is directed to the relevant in-depth references [14, 27, 28, 31].

The importance of synthesising PF-hydrolysable tannin resins is multifold. Apart from the obvious, there is a need to increase the biosourced portion of oil-derived resins and thus decrease oil dependency. There are three other factors that play a role in this development. First, the present supply of condensed tannins is relatively limited, and thus other sources of reactive polyphenolic materials are looked at, in this case hydrolysable tannins. Second, there is the need to decrease or at least maintain resin costs within today's limits due to the continuous increase in cost of oil-derived materials. Lastly, the reactivity of hydrolysable tannins being similar to that of phenol allows the use of well-developed synthetic routes to more traditional PF resins, an approach that is not possible with the far more reactive condensed tannins.

The characteristics of the PF-chestnut tannins resin prepared are: P/F ratio of 1/1.7, P:T of 70:30. The MALDI-TOF analyses were performed in positive ion modes. This article will focus on chestnut tannins monomers and dimers, and it will be considered that the main PF groups will react with chestnut monomers and dimers.

2 MATERIALS AND METHODS

2.1 Chestnut Tannin Extracts

The chestnut tannin extract used for this study is Silvafeed ENC from the company Silva Team (San Michele Mondovi', Italy). It is extracted from mature chestnut wood (*Castanea sativa*) with a hot water extraction. The extract is a brown powder, which is soluble in water, has a pH (sol. 10%) of 3.5 ± 0.5 and its relative density is between 0.5 and 0.6 kg/dm^3. This tannin contains less than 2% of fibers and more than 75% of polyphenols.

2.2 Other Materials and Their Sources

For the preparation of resins, phenol (Fisher Scientific, UK); sodium hydroxide (Carlo Erba Reagents, Italy); formaldehyde (Roth, Germany); para-formaldehyde

(Merck, Germany); methanol (VWR, Belgium) and phenolsulfonic acid at 65% weight in ethylene glycol (isomer mixture, Silvachimica Srl, Italy) were used.

For the MALDI-TOF analysis, acetone (Merck, supplied by VWR, France); 2,5-dihydroxy benzoic acid (LaserBio Labs, France); red phosphorous (LaserBio Labs, France) and sodium chloride (Carlo Erba Reagents - SdS, France) were used.

2.3 Resin Synthesis

2.3.1 Phenol-formaldehyde Control Resin, P/F Ratio of 1/1.7

A PF resin (ratio P/F of 1/1.7) was synthesised according to systems already reported by coreacting 1 mole of phenol, 0.35 mole of sodium hydroxide and 1.2 mole of formaldehyde [32]. Phenol at 80%, formaldehyde at 37% in water and sodium hydroxide at 30% in water were used.

The pH of the mixture was adjusted to 9 with 30% sodium hydroxide in water. The mixture was then slowly brought to 94°C with a water condenser and under continuous mechanical stirring. Once the temperature of 90°C was reached, the mixture was left for 2 hours. The resin was then cooled and the pH was adjusted to 7 with a 45% solution of phenolsulfonic acid in ethylene glycol. The mixture was then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

2.3.2 Phenol-formaldehyde with Chestnut Tannins Resin, P:T 70:30 and P/F Ratio of 1/1.7

For PFT resin, P:T 70:30 and P/F ratio of 1/1.7: 30% of synthetic phenol by mass was replaced with spray-dried chestnut tannin extract [11]. 148.75 g of 80% Phenol, 99.48 g of 96% paraformaldehyde powder and 45.2 g of a 30% sodium hydroxide water solution were used. First phenol and tannins (55 g) were dissolved in a water/methanol mixture (62.7 g of water/9.6 g of methanol). Paraformaldehyde was then added. This mixture was heated at 40°C for 30 minutes, with a water condenser and continuous mechanical stirring. The temperature was then increased to 94°C and 45.2 g of 30% sodium hydroxide water solution were added in four equal parts of 11.3 g each at regular intervals of 15 minutes.

After the last addition of sodium hydroxide, which occurred 45 minutes after the first addition, the mixture was further heated for 1 hour and 15 minutes to reach a total reaction time of 2 hours.

The resin was then cooled to room temperature and the pH adjusted to 7 with a 45% solution of phenolsulfonic acid in ethylene glycol. The mixture was then placed in a rotary vacuum evaporator to finally obtain a solid content of about 80% and a viscosity between 3500 and 5000 mPa.s at 25°C.

2.4 MALDI-TOF Analysis

MALDI-TOF-MS: The spectra were recorded on a SHIMADZU AXIMA Performance MALDI instrument (Manchester, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity – positive, flight path – linear, mass – high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

MALDI-TOF Sample Preparation: The samples were dissolved in acetone (4 mg/mL). The sample solutions were mixed with an acetone solution (10 mg/mL acetone) of the matrix. As the matrix, 2,5-dihydroxy benzoic acid was used. For the enhancement of ion formation, NaCl was added to the matrix (2 µL of NaCl at 0,1M in a mix of methanol:water of 2:1). The solutions of the sample and the matrix were mixed in equal amounts and 0.5 to 1 µL of the resulting solution were placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer.

3 RESULTS AND DISCUSSION

3.1 MALDI-TOF Analysis of Chestnut Tannin Extracts

By MALDI-TOF analysis, the main components found in the chestnut tannin extract used coincided with what was obtained by previous work [12, 13, *27*, *33*]. They are: gallic acid (A), glucose (B), catechin (C), ellagic acid (D), digallic acid (E), castalin (F) and castalagin (G). In this article they are identified with the letters from A to G for ease of understanding.

The peak corresponding to pure castalin is at 654 Da and the peak at 957 Da corresponds to pure castalagin. Pentagalloyl glucose (presents at 940 + 23 (Na^+) = 963 Da) and castalagin are known to be the main constituents of chestnut extract [14, 27]. These, however, were not so predominant in the analysis of the extract used where only a monomer of pentagalloyl glucose was observed and no dimer or trimer. This indicates that either the extraction was

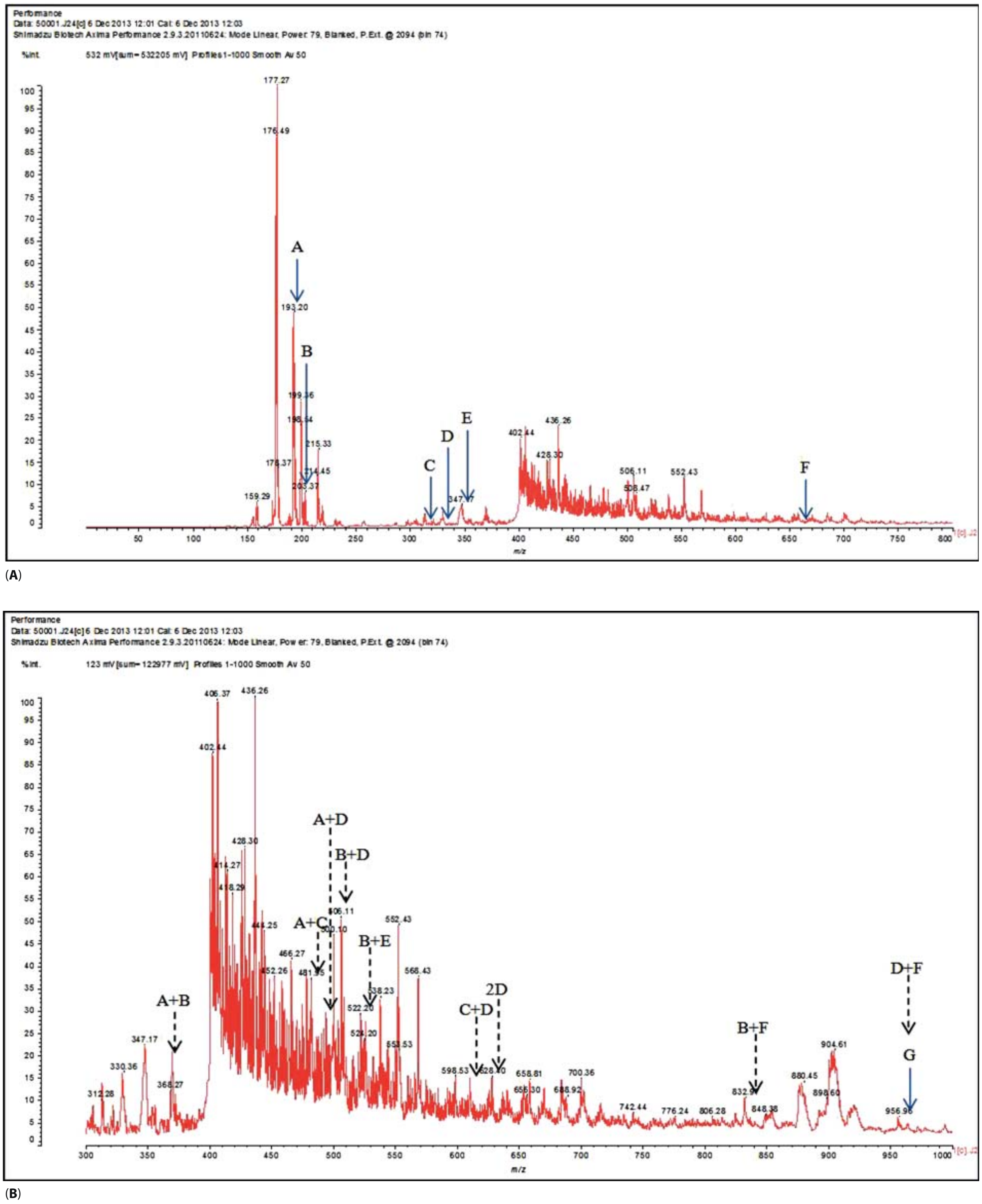


Figure 1 **(A)** Main peaks corresponding to chestnut tannins monomers (from 0 to 800 Da). **(B)** Main peaks corresponding to chestnut tannins monomers and dimers (dashed) (from 300 to 1000Da).

done under more drastic conditions or the trees were much younger than those used in previous MALDI-TOF analyses. As the extraction used for the sample used here (Silvafeed ENC) was a hot water extraction without further purification, the young age of the trees is the most likely cause. Considering all this, in the tannin extract used here the analysis showed that molecular masses were lower (Figures 1A and 1B). It was found that oligomers are linked galloyl residues with glucose [14, 27]. The peaks found were:

- 436 Da (1 galloyl residue + 2 stripped (-OHs) glucose residues);
- 506 Da (digalloylglucose = 23 (Na^+) + 152x2 + 180 = 507 Da);
- 568 Da (1 galloyl residue + 3 stripped glucose residues);
- 659 Da (trigalloylglucose, 657 Da);
- 833 Da (1 galloyl residue + 5 stripped glucose residues);
- 962 Da (pentagalloyl glucose, 963 Da).

This analysis showed that the main constituents of the chestnut tannin extract used here were gallic acid (193 Da), digallic acid (345 Da), ellagic acid (325 Da) and glucose (203 Da).

Concerning the chestnut tannins dimers found in the spectrum of the chestnut tannins used, they were mainly (in order of predominance):

- Ellagic acid-glucose (506 Da);
- Gallic acid-catechin (482 Da);
- Digallic acid-glucose (526 Da);
- Gallic acid-ellagic acid(494 Da);
- Gallic acid-digallic acid (516 Da).

3.2 MALDI-TOF Analysis of PF Control Resin

The phenol-formaldehyde resin was synthetized by basic catalysis polycondensation of phenol and formaldehyde. Reactions between phenol and formaldehyde give $-CH_2$; $-CH_2^+$ or $-CH_2OH$ groups on phenol, the main corresponding molecular weights found here are the same as those previously found and shown in Table 1 of *Schrod et al.* [*31*]. There are two repeating units; main peaks are spaced by 30 Da, or by 106 Da, which corresponds respectively to formaldehyde and $Ph\text{-}CH_2^+$, where Ph = Phenol (Figure 2).

The main phenol-formaldehyde reaction products in the PF control resin spectrum are [*31*]: $Ph\text{-}CH_2^+$ (129 Da), dimethylolphenol (177 Da), trimethylolphenol (207 Da) and $(HOCH_2)_2Ph\text{-}CH_2OCH_2OH$ (237 Da), the dimers $PhCH_2OCH_2PhCH_2OH$ (283 Da) and $HOCH_2PhCH_2PhCH_2OH$ (283 Da), $PhCH_2PhCH_2PhCH_2PhCH_2PhCH_2^+$ (554 Da), $^+H_2CPhCH_2PhCH_2Ph(CH_2^+)CH_2PhCH_2PhCH_2^+$ (580 Da).

In this article, the main phenolic components that were found in the PF control resin spectrum were identified with the letters from H to O for ease of understanding: 129 Da (H), 177 Da (I), 207 Da (J), 237 Da (K), 283 Da (L & M), 554 Da (N), 580 Da (O).

3.3 MALDI-TOF Analysis of PF-Chestnut Tannins Resin

3.3.1 *Analysis in Considering Only Chestnut Tannins Monomers/Dimers and Only PF Control Resin Groups Alone*

In Table 1 and Figure 3 are given the chestnut tannins monomers and dimers which can be found in the spectrum of the PF-chestnut tannins coreacted resin analysis. The main peaks corresponding to chestnut tannins monomers present in PF-chestnut tannins resin spectrum are: 313, 325 and 345 Da, which correspond respectively to catechin, ellagic acid and digallic acid.

Moreover, the main peaks corresponding to chestnut tannins dimers present in PF-chestnut tannins resin spectrum are: 363, 373 and 525 Da, which correspond respectively to 2xgallic acid, gallic acid-glucose and digallic acid-glucose. The main chestnut tannins monomers and dimers present in the chestnut tannin extracts spectrum are not the same as here, this indicates that there is a coreaction between phenol-formaldehyde-chestnut tannins; and even that there is no more pentagalloyl glucose.

Secondly, the presence of PF control resin groups in the spectrum of PF-chestnut tannins resin were studied; they are given in Table 1 and *Figure 3*. The main PF resin group present is that of dimethylolphenol at 177 Da. It is of interest that the dominant, purely PF oligomers present in the PF-chestnut coreacted resin are not the same as that for the pure PF resin; this also confirms that there is a definite coreaction between phenol, formaldehyde and chestnut tannin.

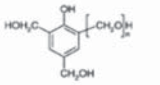
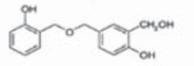
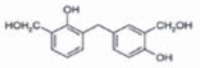
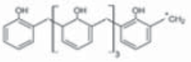
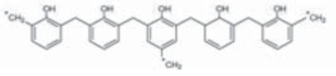
3.3.2 *Main Reactions between Chestnut Tannins Monomers/Dimers and PF Resin Groups*

This MALDI-TOF analysis confirms the coreaction between chestnut tannins, phenol and formaldehyde. This analysis in positive mode and with hydrolysable tannins shows the reactions on the phenolic components of the resin. Thus, in Table 2 and in Figure 4 are shown the oligomers of coreaction which are formed by the phenolic components of the PF resin and the chestnut tannin monomers. Considering the number of these peaks, it appears there is extensive coreaction.

In Table 3 are given the main molecular weights corresponding to the main reactions between chestnut tannins monomers and PF resin oligomers.

The main coreaction products between chestnut tannins monomers and PF compounds observed in the spectrum of the PF-chestnut tannins resin analysis are, in order of predominance: catechin-[$Ph\text{-}CH_2^+$] at 419

Table 1 Peak analysis for chestnut tannin extracts and PF control resin groups in PF-chestnut tannins resin spectrum.

Molecules	Symbols	Theoretical molecular weight & Na^+ (Da)	Molecular weight & Na^+ (Da)	
Gallic acid	A	193	193.3	Chestnut tannins monomers
Glucose	B	203	203.53	
Catechin	C	313	313.6	
Ellagic acid	D	325	331.6	
Digallic acid	E	345	343.7	
Castalagin	G	957	956.0	
2 x Gallic acid	2A	363	361.7	Chestnut tannins dimers
Gallic acid-Glucose	A+B	373	371.7	
2 x Glucose	2B	383	381.7	
Gallic acid-Ellagic acid	A+D	495	495.7	
Glucose-Ellagic acid	B+D	505	507.8	
Glucose-Digallic acid	B+E	525	525.8	
2 x Catechin	2C	603	601.8	
Catechin-Ellagic acid	C+D	615	615.9	
2 x Digallic acid	2E	667	667.9	
Ellagic acid-Castalin	D+F	957	956.0	
Digallic acid-Castalin	E+F	977	980.0	
Gallic acid-Castalagin	A+G	1127	1129.1	
Catechin-Castalagin	C+G	1247	1247.7	
Ellagic acid-Castalagin	D+G	1259	1258.8	
Digallic acid-Castalagin	E+G	1279	1282.2	
2 x Castalin	2F	1287	1289.0	
$Ph\text{-}CH_2^+$ (Ph = Phenol)	H	129	128.4	PF resin groups
Dimethylolphenol	I	177	177.5	
 where n=2	K	237	237.6	
	L	283	283.6	
	M	283	283.6	
	N	554	553.8	
	O	580	583.8	

Da, digallic acid-[$Ph\text{-}CH_2^+$] at 451 Da and gallic acid-trimethylolphenol at 377 Da.

Furthermore, belonging to the coreacted mixed species between chestnut tannins monomers and PF compounds are the series of peaks at 299, 377, 387, 419, 451, 479, 527 and 539 Da.

Concerning digallic acid, ellagic acid and catechin, they were present in this order of predominance (from the most present to the least present molecule) in the chestnut tannin extracts spectrum; however, on the PF-chestnut tannins resin spectrum they are in the opposite order. So it can be said that digallic acid has coreacted more with phenol-formaldehyde compounds than ellagic acid and even much more than catechin. This can be explained by the lower proportion of reactable sites of ellagic acid than digallic acid. But the hypothesis is not so evident because normally catechin is activated more by the OHs groups than digallic and ellagic acids. Maybe the molecules of catechin are blocked by the reactions of catechin with itself or with other chestnut tannins monomers, and that is why catechin does not react with phenol and formaldehyde.

The peak at 525 Da belongs to the reaction product between catechin and two molecules of $Ph\text{-}CH_2^+$. There are two main possibilities by which the copolymerisation can take place. In the first one, one $Ph\text{-}CH_2^+$ attacks the site 6 of the aromatic ring A of catechin and the other $Ph\text{-}CH_2^+$ attacks the site 8 of the aromatic ring A. The second possibility is that both $Ph\text{-}CH_2^+$ molecules coreact together and then attack the site 6

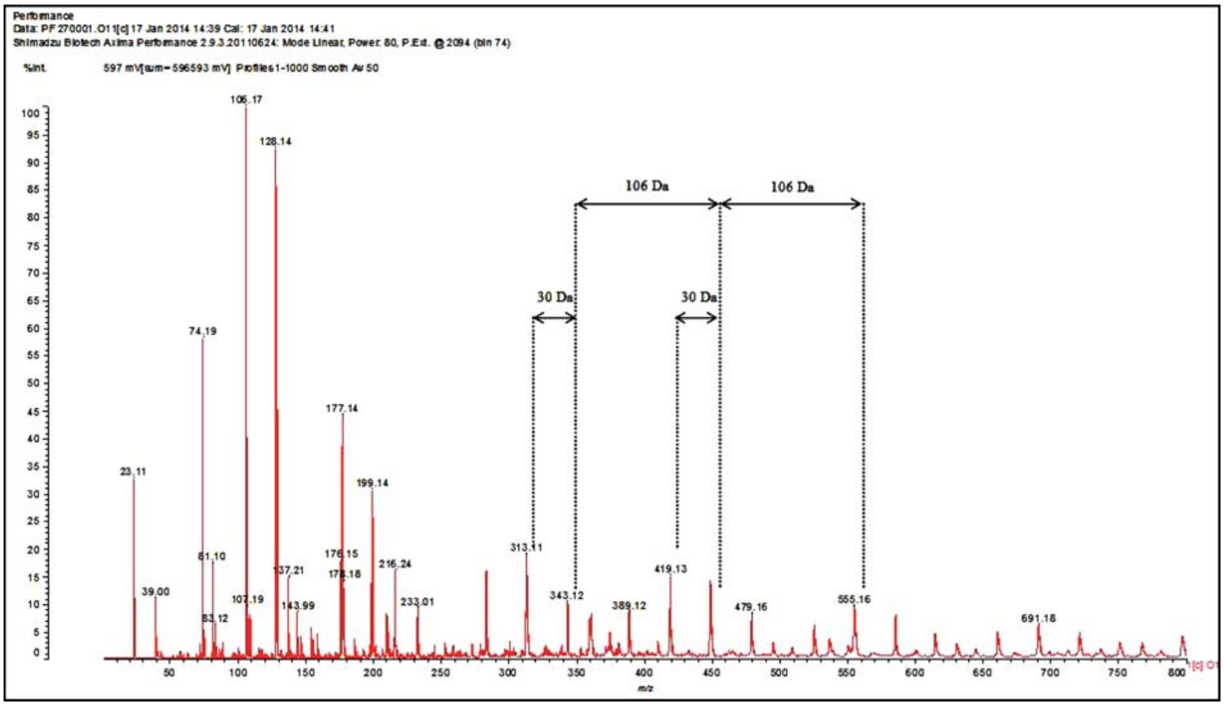


Figure 2 Spectrum of PF resin.

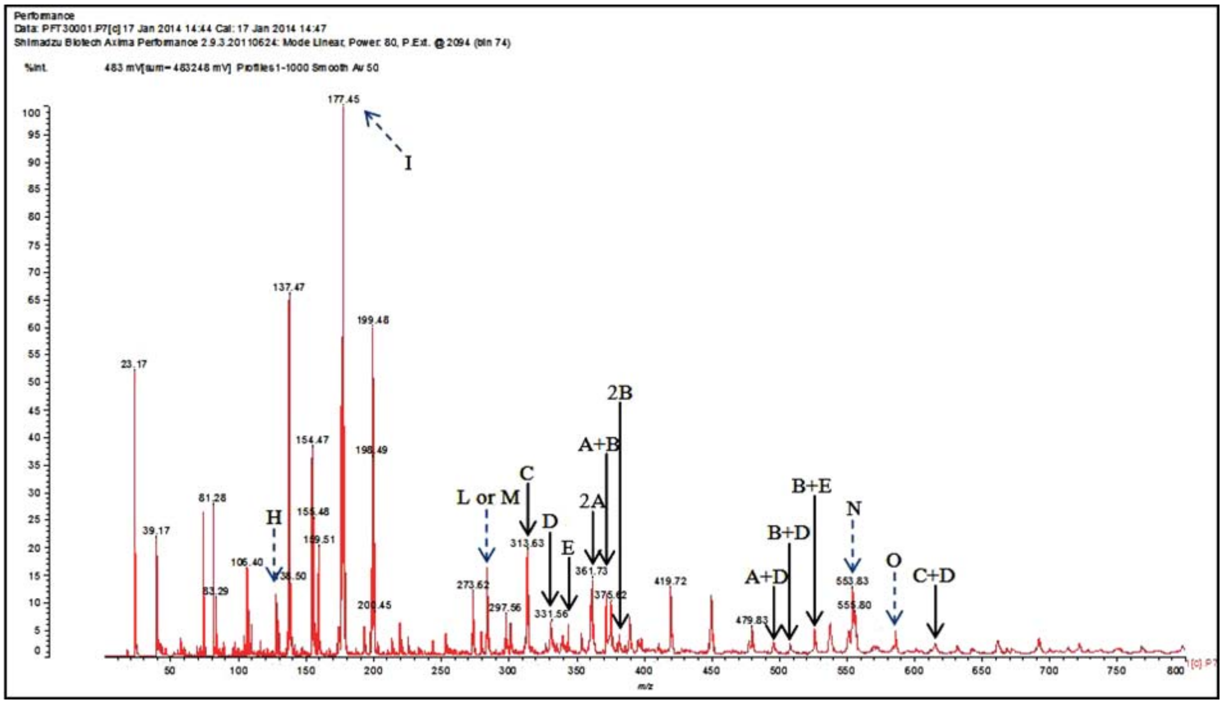
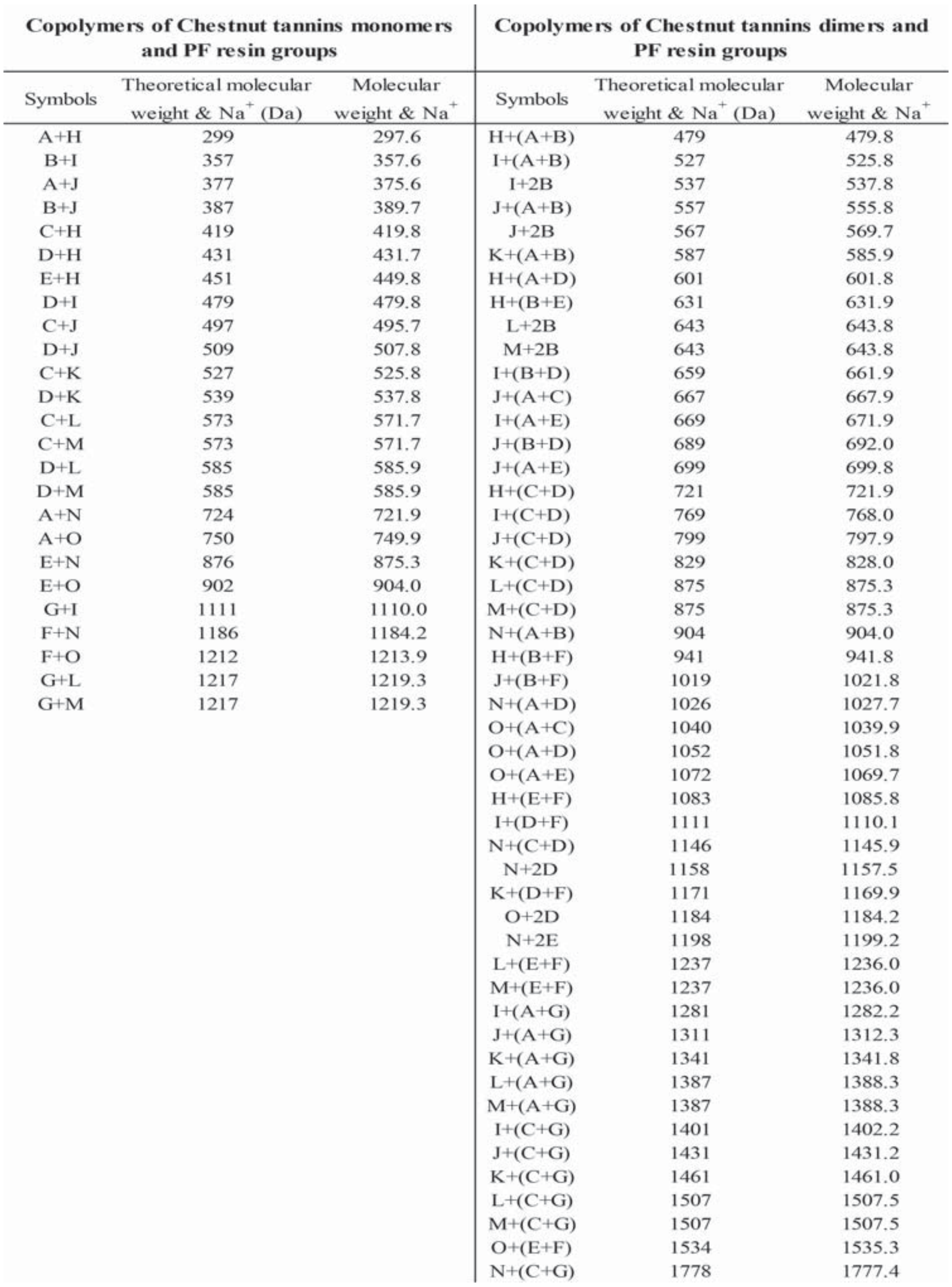


Figure 3 Main peaks corresponding to PF control resin groups alone (dashed) and key peaks corresponding to main chestnut tannins monomers and dimers alone in PF-chestnut tannins resin spectrum.

Table 2 Copolymer peaks analysis for reactions between chestnut tannins monomers/dimers and PF resin groups in PF-chestnut tannins resin spectrum.



Copolymers of Chestnut tannins monomers and PF resin groups			**Copolymers of Chestnut tannins dimers and PF resin groups**		
Symbols	Theoretical molecular weight & Na$^+$ (Da)	Molecular weight & Na$^+$	Symbols	Theoretical molecular weight & Na$^+$ (Da)	Molecular weight & Na$^+$
A+H	299	297.6	H+(A+B)	479	479.8
B+I	357	357.6	I+(A+B)	527	525.8
A+J	377	375.6	I+2B	537	537.8
B+J	387	389.7	J+(A+B)	557	555.8
C+H	419	419.8	J+2B	567	569.7
D+H	431	431.7	K+(A+B)	587	585.9
E+H	451	449.8	H+(A+D)	601	601.8
D+I	479	479.8	H+(B+E)	631	631.9
C+J	497	495.7	L+2B	643	643.8
D+J	509	507.8	M+2B	643	643.8
C+K	527	525.8	I+(B+D)	659	661.9
D+K	539	537.8	J+(A+C)	667	667.9
C+L	573	571.7	I+(A+E)	669	671.9
C+M	573	571.7	J+(B+D)	689	692.0
D+L	585	585.9	J+(A+E)	699	699.8
D+M	585	585.9	H+(C+D)	721	721.9
A+N	724	721.9	I+(C+D)	769	768.0
A+O	750	749.9	J+(C+D)	799	797.9
E+N	876	875.3	K+(C+D)	829	828.0
E+O	902	904.0	L+(C+D)	875	875.3
G+I	1111	1110.0	M+(C+D)	875	875.3
F+N	1186	1184.2	N+(A+B)	904	904.0
F+O	1212	1213.9	H+(B+F)	941	941.8
G+L	1217	1219.3	J+(B+F)	1019	1021.8
G+M	1217	1219.3	N+(A+D)	1026	1027.7
			O+(A+C)	1040	1039.9
			O+(A+D)	1052	1051.8
			O+(A+E)	1072	1069.7
			H+(E+F)	1083	1085.8
			I+(D+F)	1111	1110.1
			N+(C+D)	1146	1145.9
			N+2D	1158	1157.5
			K+(D+F)	1171	1169.9
			O+2D	1184	1184.2
			N+2E	1198	1199.2
			L+(E+F)	1237	1236.0
			M+(E+F)	1237	1236.0
			I+(A+G)	1281	1282.2
			J+(A+G)	1311	1312.3
			K+(A+G)	1341	1341.8
			L+(A+G)	1387	1388.3
			M+(A+G)	1387	1388.3
			I+(C+G)	1401	1402.2
			J+(C+G)	1431	1431.2
			K+(C+G)	1461	1461.0
			L+(C+G)	1507	1507.5
			M+(C+G)	1507	1507.5
			O+(E+F)	1534	1535.3
			N+(C+G)	1778	1777.4

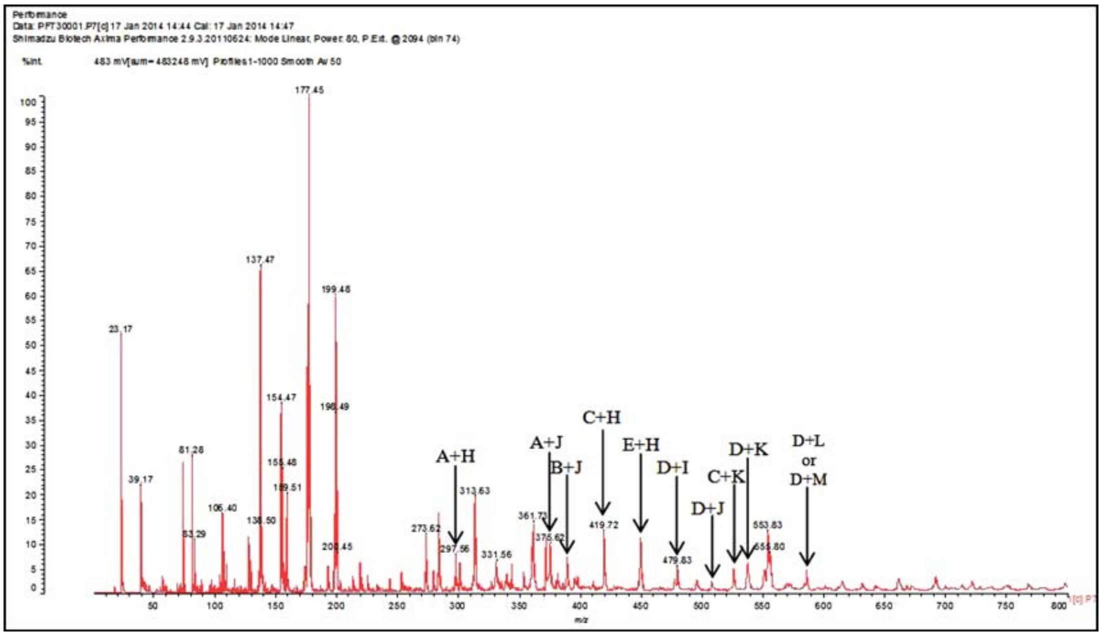
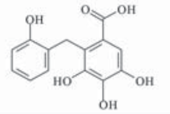
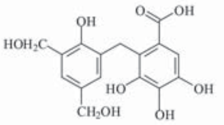
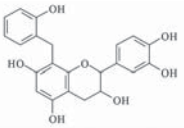
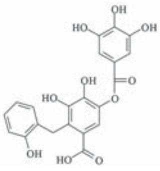
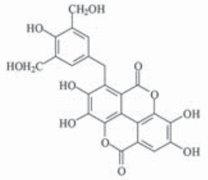


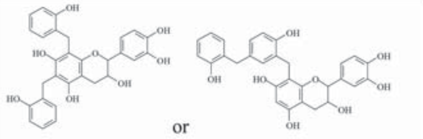
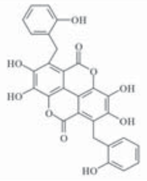
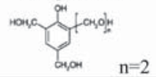
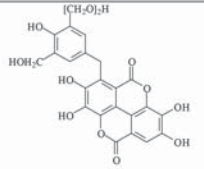
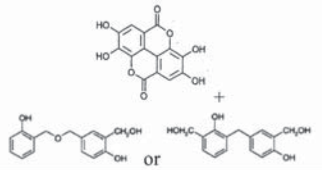
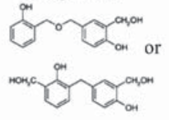
Figure 4 Main peaks corresponding to reactions between chestnut tannins monomers and PF resin groups in PF-chestnut tannins resin spectrum.

Table 3 Peaks corresponding to the molecular weights of main reactions between chestnut tannins and PF resin groups (Ph = Phenol) in PF-chestnut tannins resin spectrum.

Read molecular weight (Da)	*Theoretical molecular weight (Da)*	*Molecules*	*Indications*
297.6	299		Gallic acid + Ph-CH_2^+
375.6	377		Gallic acid + Trimethylolphenol
389.7	387	203 + 184	Glucose + Trimethylolphenol
419.7	419		Catechin + Ph-CH_2^+
449.8	451		Digallic acid + Ph-CH_2^+
479.8	479		Ellagic acid + Dimethylolphenol

(*Continued*)

Table 3 (cont.)

525.8	525		Catechin + 2 x Ph-CH$_2^+$
537.8	537		Ellagic acid + 2 x Ph-CH$_2^+$
537.8	539		Ellagic acid + 
			
555.8	557	450 + Ph-CH$_2^+$	Digallic acid + 2 x Ph-CH$_2^+$
585.9	585		Ellagic acid + 
631.9	631	419 + 2 x Ph-CH$_2^+$	Catechin + 3 x Ph-CH$_2^+$
631.9	633	479 + Dimethylolphenol	Ellagic acid + 2 x Dimethylolphenol
661.9	663	451 + 2 x Ph-CH$_2^+$	Digallic acid + 3 x Ph-CH$_2^+$

of the aromatic ring A. So both isomers can be formed during the copolymerisation of chestnut tannins, phenol and formaldehyde.

Concerning the reactions between chestnut tannin dimers and PF compounds, the molecular weights of these copolymers are shown in Table 2 and Figures 5A and 5B. It was chosen to only consider chestnut tannins dimers which are present in the spectrum of chestnut tannin extract. Indeed, the molecular weights present are quite low, with no more peaks above 930 Da.

The main reactions between chestnut tannins dimers and PF resin groups which can be found in the spectrum of PF-chestnut tannins resin analysis are given in Table 2. The products of coreaction are, in order of predominance: trimethylolphenol-(gallic acid-glucose) at 557 Da, dimethylolphenol-2xglucose at 537 Da and dimethylolphenol-(gallic acid-glucose) at 527 Da. The series of peaks at 479, 527, 537, 557 and 587 Da belongs to the coreacted mixed species between chestnut tannins dimers and PF compounds.

Gallic acid, which is in practice the majority component in the analysis of chestnut tannin extract, is now almost depleted and its proportion is small. As it is also still present in the main coreactions between phenol, formaldehyde and chestnut tannin, it is clearly the main unit in the reactions of chestnut tannin with the PF compounds.

There are an important number of peaks in this MALDI-TOF analysis, and even if these are not so intense (even a few percent), they should not be disregarded. They show us that many coreactions take place between chestnut tannins, phenol and formaldehyde.

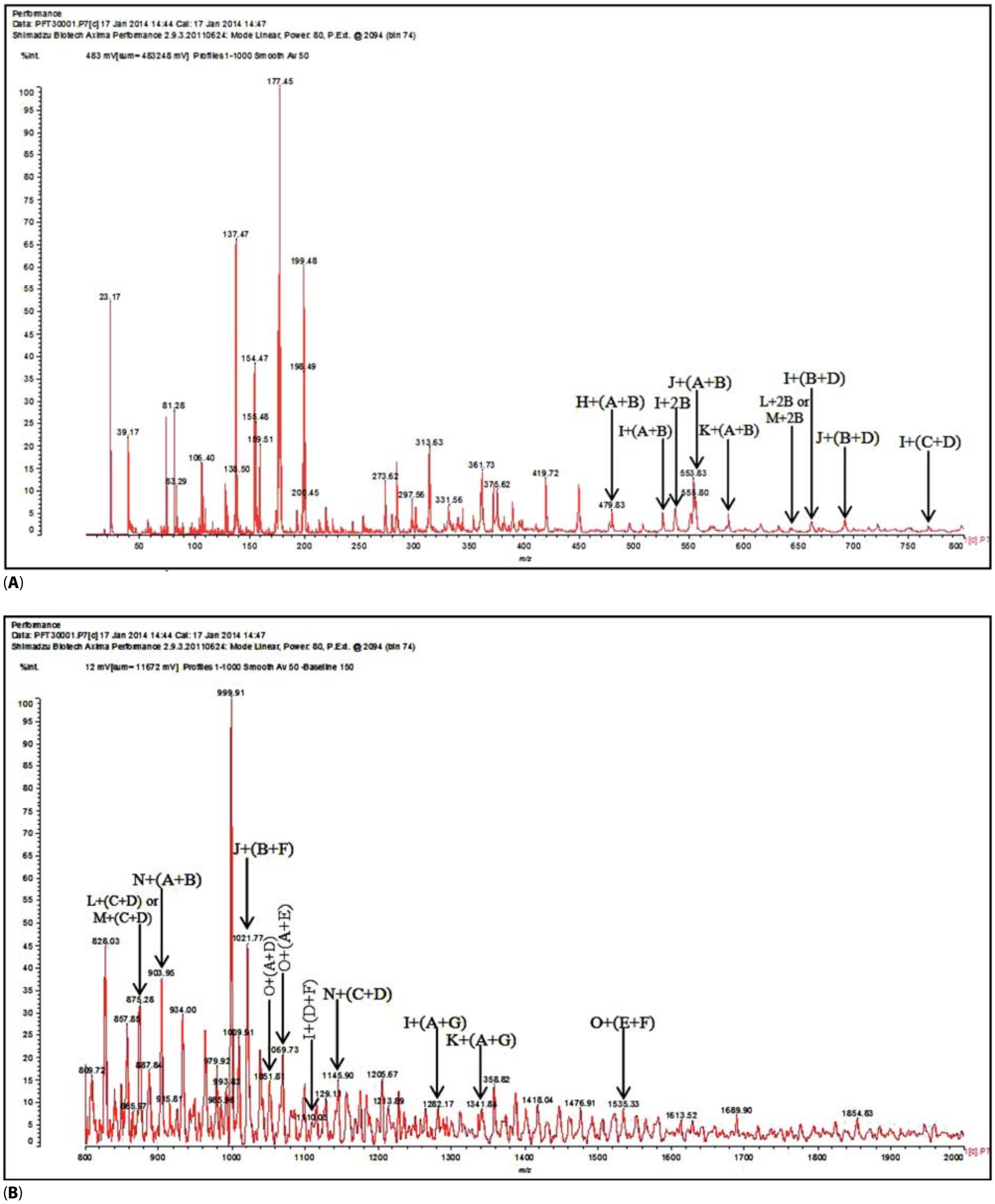


Figure 5 (A) Main peaks corresponding to reactions between chestnut tannins dimers and PF resin groups in PF-chestnut tannins resin spectrum (from 0 to 800 Da). **(B)** Main peaks corresponding to reactions between chestnut tannins dimers and PF resin groups in PF-chestnut tannins resin spectrum (from 800 to 2000 Da).

4 CONCLUSIONS

MALDI-TOF analyses confirm previous knowledge about the structures involved in commercial chestnut gallo/ellagitannins, and for the first time, in complex tannins. The known rearrangements caused by the extraction clearly appear to occur as castalin, castalagin and pentagalloyl glucose are present, but in smaller proportions than expected, indicating strong hydrolysis during the extraction of the particular chestnut tannin extract used. The chestnut tannin extract used has been found to be composed mainly of gallic acid, digallic acid, ellagic acid and glucose.

Coreaction between PF oligomers and chestnut tannins occurs extensively and yields many possible combinations. Even for one molecular mass there can be different possibilities of reactions like, for example, for the peak at 479 Da.

Even if hydrolysable tannin aromatic rings are less reactive than the reactive sites of phenol, it has been shown that hydrolysable/complex chestnut tannins coreact with formaldehyde, forming methylene bridges linking phenol and the phenolic rings of tannins. These methylene bridges are formed between the ortho and para sites of the synthetic phenol and the meta sites of the gallic acid. As these meta sites are rather sterically hindered, it can be concluded that the main coreaction is between the methylol group formed on the PF oligomers and the aromatic rings in chestnut tannin.

Thus, hydrolysable/complex chestnut tannins are able to substitute a high proportion of synthetic phenol in PF resins for different applications, for example, foam wood particleboard adhesives or even foams.

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