

Structural diversity of nucleophilic adducts from flavanols and oak wood aldehydes

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Abstract

The reactions between (+)-catechin and a representative oak wood aldehyde (furfuraldehyde, 5-(hydroxymethyl)furfuraldehyde, 5-methylfurfuraldehyde, vanillin, or syringaldehyde) in a wine-like model solution were studied and the formed condensation products were characterized by LC/MS and LC/MS/MS.

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Keywords: Procyanidins; Oak wood aldehydes; HPLC/UV–Visible; LC/ESI-MS; MS/MS

1. Introduction

Procyanidins extracted from grapes contribute to young red wines' astringency. These procyanidins are polymers of flavanol units with C4–C6 or C4–C8 linkages. Aging wine in oak barrels for several months is a procedure commonly employed by winemakers in order to improve quality. During this period, the wood transfers phenolic (vanillin and syringaldehyde) and furanic (furfuraldehyde, 5-(hydroxymethyl)furfuraldehyde, 5-methylfurfuraldehyde) aldehydes as well as ellagitannins to the wine, directly contributing to wine aroma and taste. Lignins and polysaccharides are the source of the aldehydes in the toasted oak wood (Nonier et al., 2006)

The contribution of aldehydes, in general, and acetaldehyde in particular, is now well characterized: they are able to react with flavanols (Fulcrand, Docco, Es-Safi, Cheynier, & Moutounet, 1996a; Saucier, Bourgeois, Vitry, Roux, &

Glories, 1997) and/or anthocyanidins (Escribano-Baillon, Dangles, & Brouillard, 1996; Fulcrand, Cameira dos Santos, Sarni-Manchado, Cheynier, & Favre-Bonvin, 1996b; Timberlake & Bridle, 1976) through a Bayer acid-catalyzed condensation (Bendz, Martensson, & Nilsson, 1967), giving access to a condensation product composed of two flavanols (or one flavanol and one anthocyanidin) linked by a chemical bridge depending on the aldehyde used for the reaction. Such condensation products have been already detected in wine where they are thought to intervene in red wine colour and astringency evolution (Atanasova, Fulcrand, Le Guernevé, Cheynier, & Moutounet, 2002; Fulcrand et al., 1996a; Herjavec, Jeromel, Da Silva, Orlic, & Redzepovic, 2007; Mateus, Silva, Rivas-Gonzolo, Santos Buelga, & De Freitas, 2002; Towel & Waterhouse, 1996). During wine aging, condensation reactions are known to occur with aldehydes released from oak barrels (De Freitas, Sousa, Silva, Santos-Buelga, & Mateus, 2004; Es-Safi, Cheynier, & Moutounet, 2000; Sousa, Mateus, Perez-Alonso, Santos-Buelga, & De Freitas, 2005).

In a relatively recent work, the kinetic at pH 3 and pH 3.5 was studied. A comparative study on the reactivity of the two representative families of aldehydes (phenolic and

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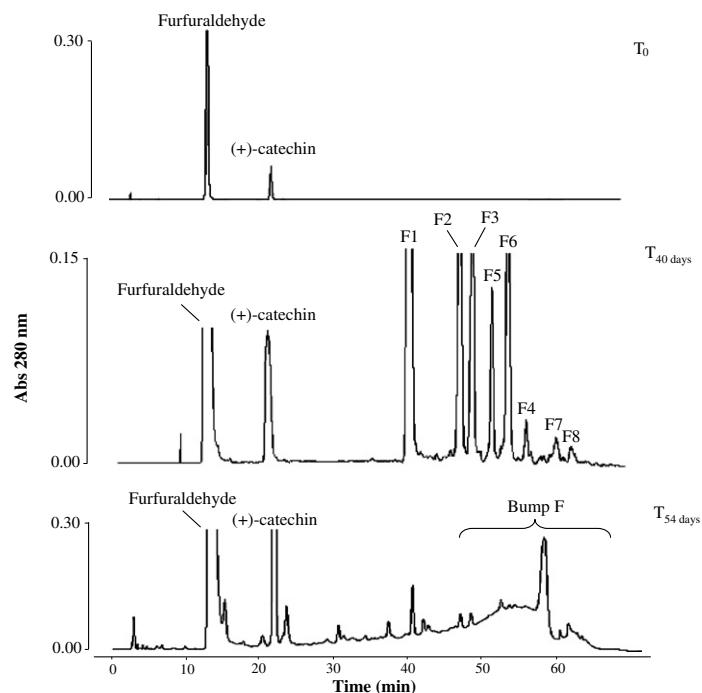


Fig. 1. HPLC chromatogram at 280 nm during the furfuraldehyde/(+)-catechin reaction performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

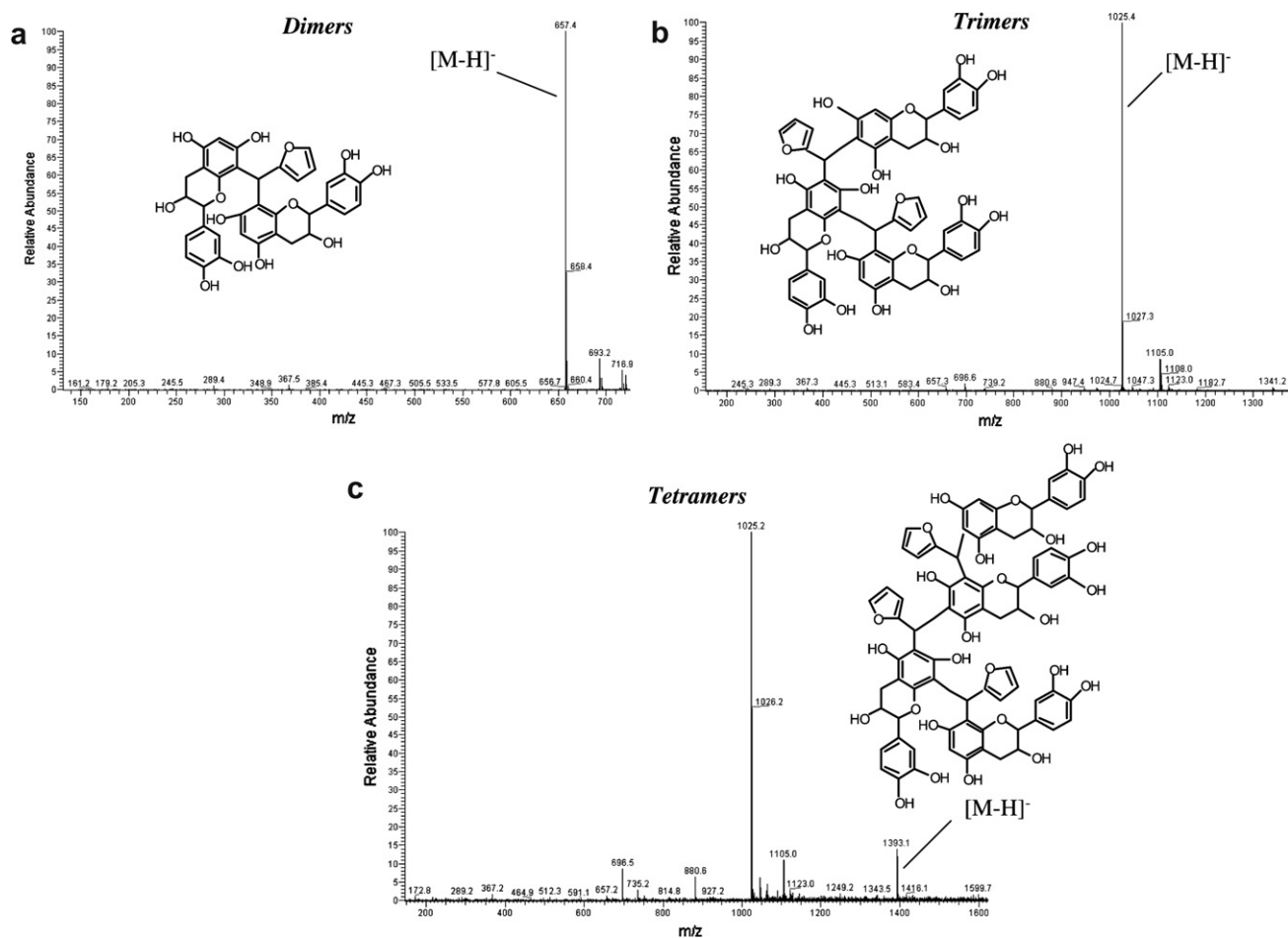


Fig. 2. Mass spectra of (a) dimer adduct of catechin–furfuraldehyde, (b) trimer adduct of catechin–furfuraldehyde and (c) tetramer adduct of catechin–furfuraldehyde.

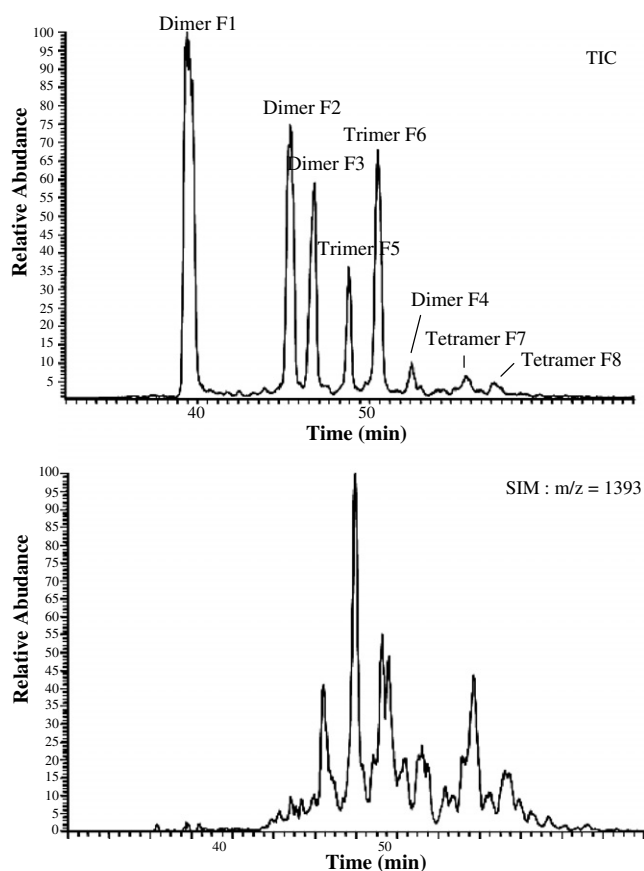


Fig. 3. Single ion monitoring chromatogram at m/z 1393 during the furfuraldehyde/(+)-catechin reaction performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

furanic aldehydes) on (+)-catechin is presented: a great difference of reactivity between the two types of aldehydes was studied (Nonier, Vivas, Vivas de Gaulejac, Pianet, & Fouquet, 2007).

The aim of the present work was to study by LC/MS the condensation products of flavanols with the different oak wood aldehydes in model solution systems.

The implication of these reactions and these new products on the sensorial and colour properties of wines are also discussed.

2. Materials and methods

2.1. Reagents

Deionized water was purified with a Milli-Q system (Millipore, Bedford, MA) prior to use. Methanol and formic acid were obtained from Prolabo (Pessac, France). Acetonitrile was purchased from Prolabo (Pessac, France). (+)-Catechin, acetaldehyde, furfuraldehyde, 5-(hydroxymethyl)furfuraldehyde (HMF), and 5-methylfurfuraldehyde were purchased from Aldrich (Saint-Quentin, France).

2.2. Reactions

To investigate the reaction between flavanols and oak wood aldehydes, (+)-catechin was separately incubated with furfuraldehyde, 5-(hydroxymethyl)furfuraldehyde, 5-methylfurfuraldehyde, vanillin and syringaldehyde at pH 3.5. The formed compounds were monitored by HPLC

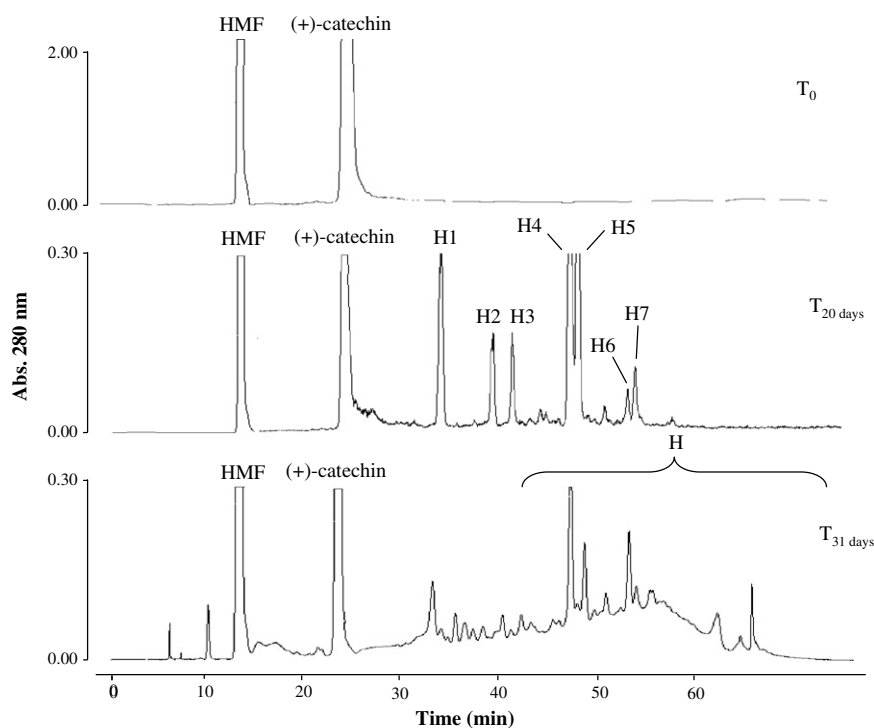


Fig. 4. HPLC chromatogram at 280 nm during the hydroxymethylfurfuraldehyde/(+)-catechin reaction performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

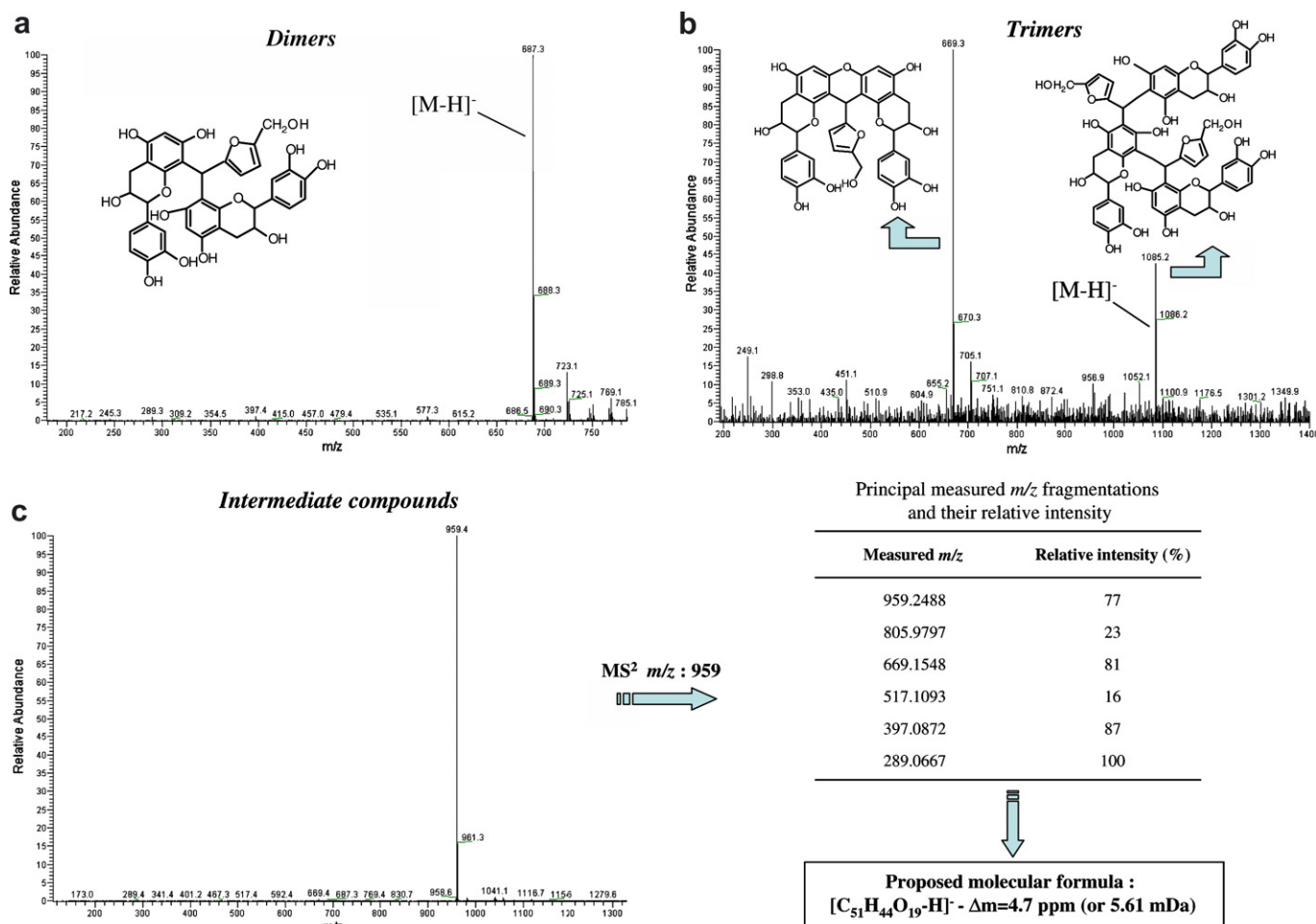


Fig. 5. Mass spectra of (a) dimer adduct of catechin–HMF, (b) trimer adduct of catechin–HMF and (c) intermediate compound of catechin–HMF, and the principal measured *m/z* in MS² mode (ion *m/z*: 959).

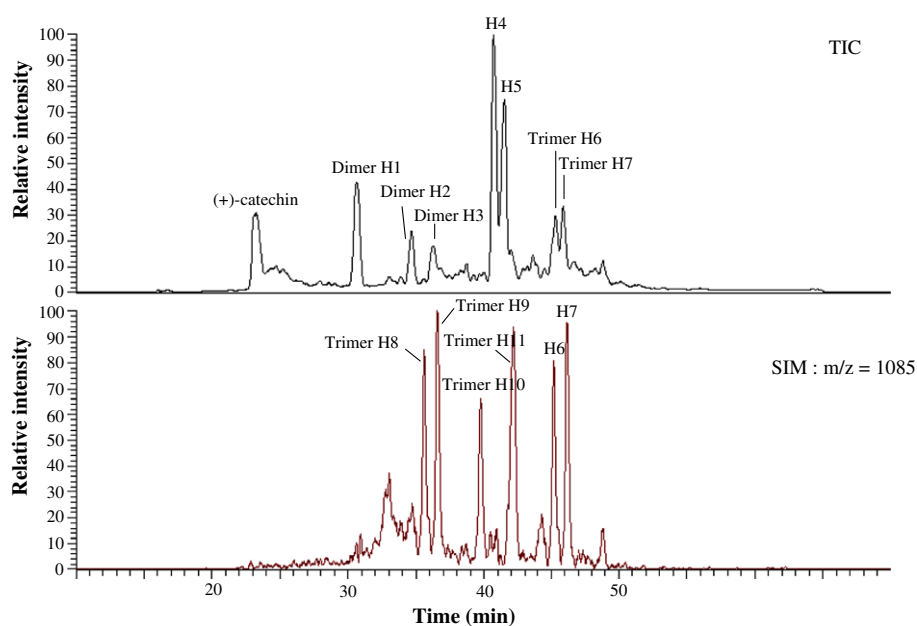


Fig. 6. Single ion monitoring chromatogram at *m/z* 1085 during the HMF/(+)-catechin reaction performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

with UV–Visible and diode array detection, and characterized by LC/ESI-MS.

The model wine solution used was 12% EtOH buffered to pH 3.5 (5 g/L tartaric acid, 1 N NaOH to pH 3.5). (+)-Catechin (1.65 mM) was prepared in each resulting solution (50 mL). The aldehydic derivatives (acetaldehyde, furfuraldehyde, 5-(hydroxymethyl)-furfuraldehyde, 5-methylfurfuraldehyde, vanillin, syringaldehyde) were added at a concentration of 3.14 mM. The prepared solutions were incubated at 20 °C and in the absence of light. Reactions were periodically monitored by liquid chromatography (LC) coupled with an UV detector and with an electrospray mass spectrometry (ESI-MS) detector during a period varying according to the nature of the aldehyde. Quantification of residual (+)-catechin and of all formed compounds was achieved on the basis of peak areas at 280 nm. Identification of the formed products was achieved on the basis of their UV–Visible and MS spectrum and by comparison with standards.

There was a control included of catechin with no aldehyde compound: there is no modification of the composition of the solution (data not shown).

The samples were prepared and subsequently analyzed in replicate (data not shown).

2.3. HPLC/UV–Visible analysis

HPLC/UV–Visible analyses were performed with a Waters separation module system, a Waters UV–Visible

detector, and Millennium32 chromatography manager software. UV–Visible spectra were recorded at 280 nm and 440 nm. The column was a reverse-phase Interchim C18 (10 μ m packing, 250 \times 4.7 mm i.d.) protected with a guard column of the same material; solvent A, water/formic acid (98:2, v/v); solvent B, acetonitrile/water/formic acid (80:18:2, v/v). The elution program was performed at a constant flow of 1 ml/min, passing from 5% to 30% of B in 40 min, and then rising to 40% of B in 10 min, and finally to 100% of B in 5 min, followed by washing and re-equilibrating the column during 15 min. The injection volume was 20 μ l.

2.4. LC/ESI-MS analysis

MS measurements were performed on a ion trap instrument with an electrospray ionization source. The mass spectrometer was operated in negative ion mode. Ion spray voltage was selected at 4.5 kV and the capillary temperature was selected at 275 °C.

Conditions of HPLC were identical to those described above.

3. Results and discussion

3.1. Reactions with furfuraldehyde

HPLC (Fig. 1) technique permitted us to follow the reaction between (+)-catechin and furfuraldehyde. HPLC/DAD analysis of the mixture showed the presence

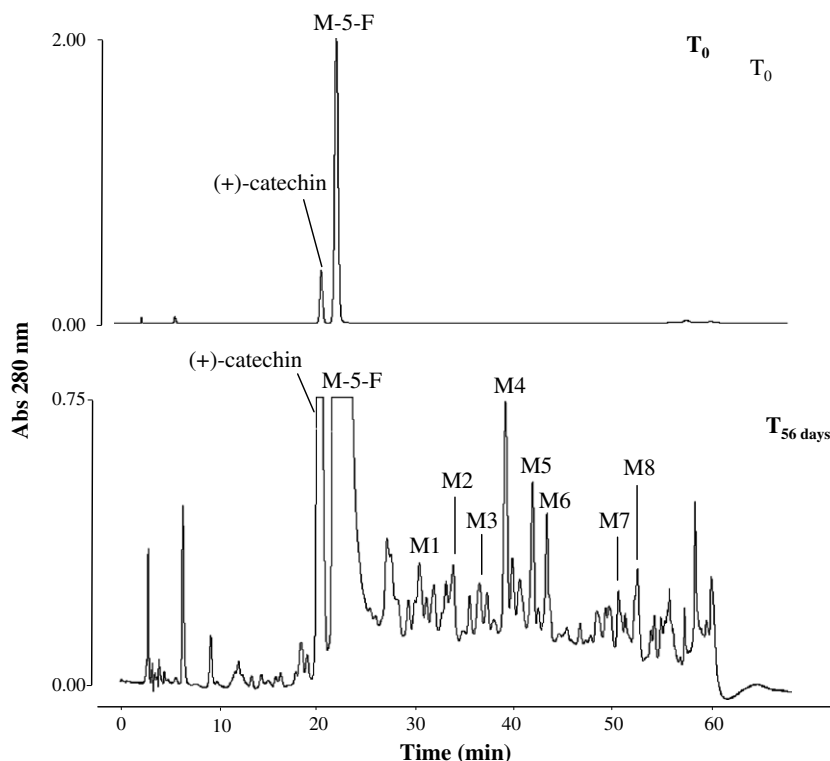


Fig. 7. HPLC chromatogram at 280 nm during the methyl-5-furfuraldehyde/catechin reaction. Reaction was performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

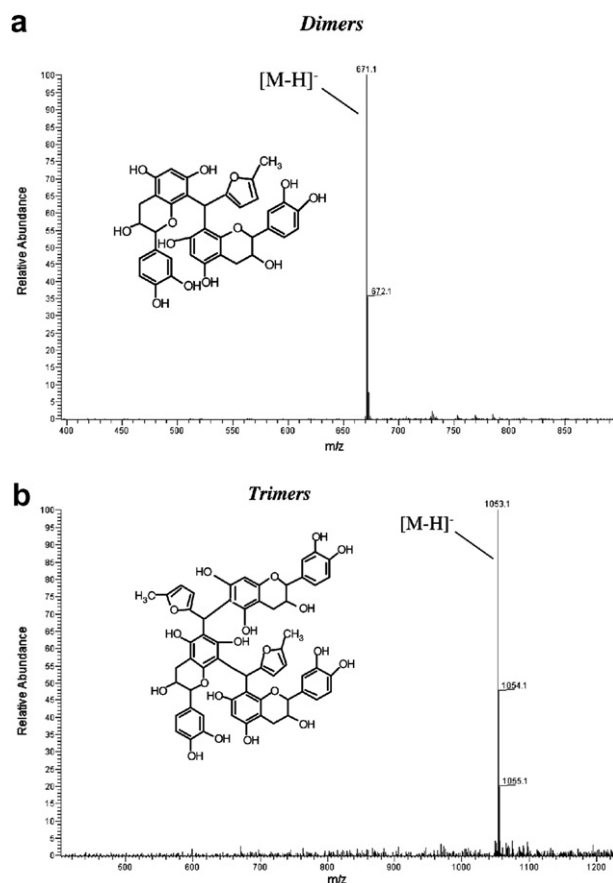


Fig. 8. Mass spectra of (a) dimer adduct of catechin-M-5-F, (b) trimer adduct of catechin-M-5-F.

of additional peaks (F1, F2, F3, F4, F5, F6, F7 and F8) in addition to (+)-catechin and furfuraldehyde (Fig. 1), indicating that a reaction between (+)-catechin and furfural occurred.

The first two peaks on the chromatogram correspond to furfuraldehyde and (+) catechin, respectively, and the others are condensed products of (+)-catechin and furfuraldehyde.

LC/MS analysis, performed in the negative ion mode, allowed molecular weight determination of the first four products formed through this reaction. The obtained results indicated that these products were oligomeric derivatives consisting of (+)-catechin units bridged by furfuryl groups formed according to the mechanism previously postulated by Timberlake and Bridle⁴ in the case of acetaldehyde. The m/z values of compounds F1, F2, F3 and F4 detected at (Fig. 2a) showed that the constitutive units were linked by furfuryl bridges. Mass spectrometric analysis revealed thus that compounds F1, F2, F3 and F4 all have molecular weights of 658 and corresponded to two (+)-catechin linked by a furfuryl bridge.

HPLC/UV at 280 nm and LC/MS analysis in negative mode, at 40 days of reaction, revealed the presence of two compounds (F5, F6): all had molecular weights of 1026 amu ($[M-H]^-$ ion signals at m/z 1025) (Fig. 2b) and corresponded to a structure in which three (+)-catechin are linked by two furfuryl bridges. They are trimer adducts.

And on the other hand, these analysis revealed the presence of two other peaks (F7, F8) which had molecular weight of 1394 amu ($[M-H]^-$ ion signals at m/z

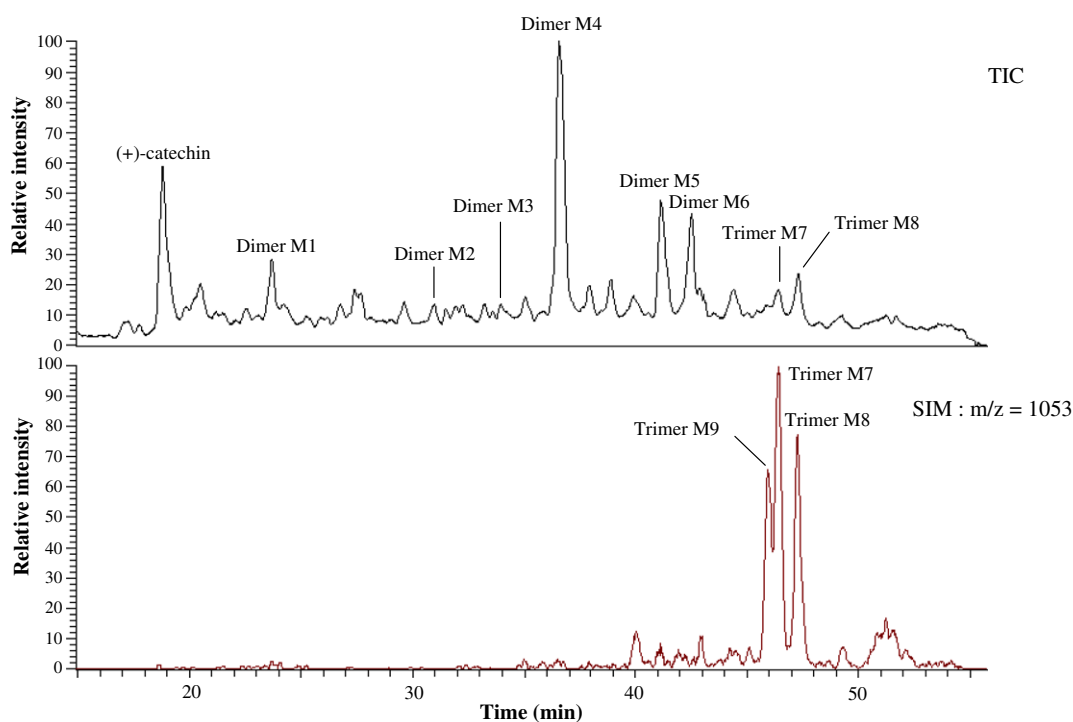


Fig. 9. Single ion monitoring chromatogram at m/z 1053 during the M-5-F/(+)-catechin reaction performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

1393 amu) (Fig. 2c) and corresponded to a structure in which four (+)-catechin are linked by three furfuryl bridges. They are tetramer adducts.

Complementary analysis, in LC/MS, and more exactly in single ion monitoring (SIM) were conducted. They permitted to observe peaks not detectable in LC/DAD. Fig. 3 presented the total ion chromatogram (TIC) at 40 days of reaction and the corresponding chromatogram in SIM mode: the selected ion was m/z 1393 amu corresponding to the tetramer. We observed on the SIM chromatogram five peaks corresponding to tetramer, and which were not observable on the TIC.

Actually, experiments are conducted to characterize polymerized forms (bump F) improving LC/MS technique.

After 15 days of reaction, F1, F2, and F3 reached their maximum concentrations. After 27 days of reaction, the quantity of F1, F2, F3, F4 products decreased considerably and other compounds were formed (F5, F6, F7, F8), with longer retention times corresponding to polymerized compounds. This was confirmed by the appearance of a bump at the end of the chromatogram profile which showed that the reaction evolved to more

polymerized compounds which finally precipitated as a black solid in the test tube.

Es-Safi et al. (2000) described the formation of a bump at the end of the chromatogram, when the reaction between (+)-catechin and furfuraldehyde was finished. It was not surprising to observe the formation of polymerized forms because the reactions of polymerization between flavonoids and furfuraldehyde in acid medium (relevant to wine pH) had been demonstrated and have been used for the production of organic aerogels (Hubresch, 1994).

Fig. 1 shows that when the quantity of dimers, trimers and tetramers F1, F2, F3, F4, F5, F6, F7 and F8 decreased, the size of the bump increased. This is in agreement with the reactional scheme, which demonstrates that dimers are consumed in the polymerization reaction.

3.2. Reactions with hydroxymethylfurfuraldehyde (HMF)

When (+)-catechin was incubated in the presence of HMF, a reaction between these two reactants occurred with the formation of analogous oligomeric compounds (Fig. 4), with greater quantities for each of them. During

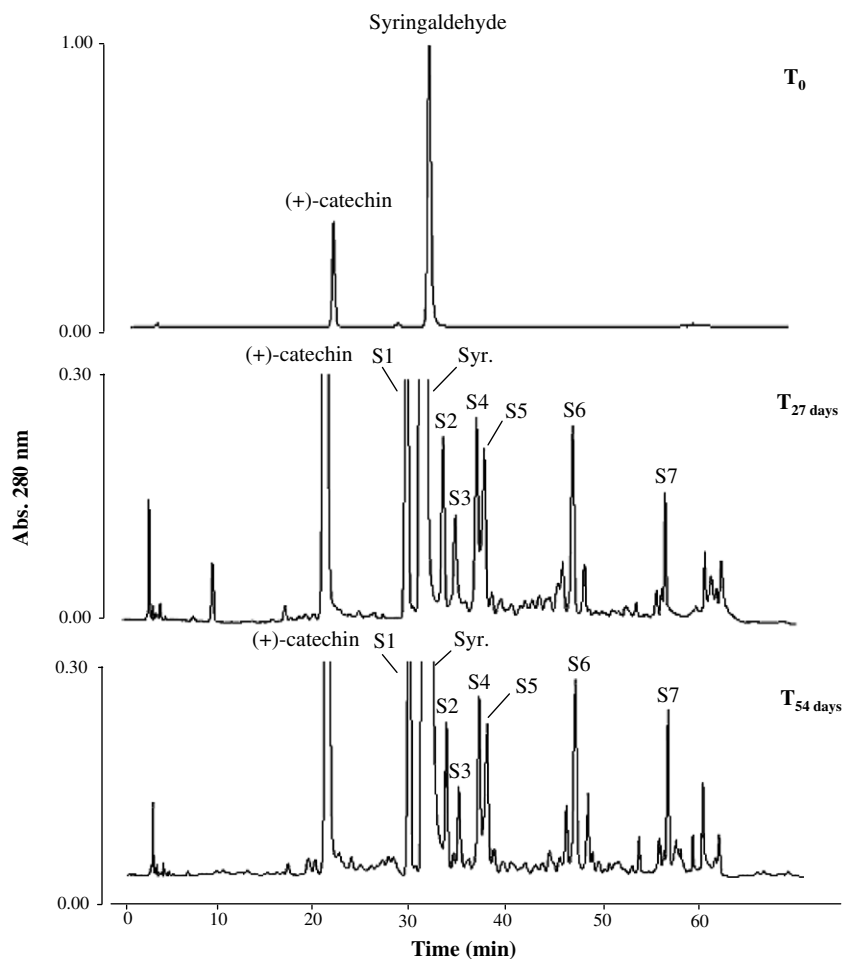


Fig. 10. HPLC chromatogram at 280 nm during the syringaldehyde/catechin reaction. Reaction was performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

the first days, when (+)-catechin was incubated with HMF, the decrease of catechin was accompanied by a large non-resolved group of peaks (H) (Fig. 4). This peak has a maximum area at 17 days of reaction, before decreasing.

LC/MS analysis, conducted in the negative ion mode, allowed molecular weight determination of the seven products formed through this reaction. Mass spectrometric analysis revealed that the compounds H1, H2, H3 gave all $[M-H]^-$ ion signals at m/z 687 as shown on the obtained mass spectrum (Fig. 5a). Their molecular weight (688 amu) corresponds exactly to a structure in which two (+)-catechin units are linked by a hydroxymethylfurfuryl.

Mass spectrometry analysis revealed also the presence of that the two new compounds H6 and H7 all had molecular weights of 1086 amu ($[M-H]^-$ ion signals at m/z 1085 amu) (Fig. 5b) and corresponded to a structure in which three (+)-catechin are linked by two hydroxymethylfurfuryl bridge. They are trimer adducts.

The m/z values of compounds H4 and H5 detected at m/z 959 amu (Fig. 5c) did not permit to establish the structure of these compounds: MS² analysis was conducted. Mass exact were performed on a Q-ToF instrument. Fig. 5c presented the measured m/z and their corresponding relative intensity. An hypothetical molecular formula was presented: $[C_{51}H_{44}O_{19}-H]^-$, with a Δm (error) = 4.7 ppm (or 5.61 mDa).

The mass value at m/z 669 amu could correspond to a xanthene adduct in a mixture of (+)-catechin and hydroxymethylfurfuraldehyde according to the structure proposed by Es-Safi et al. (2000) (structure presented in Fig. 5b). The difference between mass values at m/z 959 and m/z 669 corresponds to the lost of one catechin unit. It is very possible that the compounds H4 and H5 are composed by three catechin units and a hydroxymethylfurfuryl bridge: [catechin–catechin–hydroxymethylfurfuryl–catechin].

The non-resolved group of peaks (H) at the end of the chromatogram were not ionisable under the conditions adopted in this experiment.

Complementary analysis, in LC/MS, and more exactly in single ion monitoring (SIM) were conducted. They permitted to observe peaks no detectable in LC/DAD. Fig. 6 presented the total ion chromatogram (TIC) at 20 days of reaction and the corresponding chromatogram in SIM mode: the selected ion was 1085 corresponding to the trimer. We observed on the SIM chromatogram four peaks (H8, H9, H10, H11) corresponding to trimer, and which were not observable on the TIC.

The bump observed at the end of the chromatogram in the case of furfuraldehyde also appeared in the case of HMF (data not shown), but its presence was only detected from 30 days at pH 3.5, compared with 12 days in the case of furfuraldehyde. After 70 days of reaction, no precipitate was observed in the vial at pH 3.5; so the polymerization was more difficult to occur.

3.3. Reactions with methyl-5-furfuraldehyde (M-5-F)

HPLC/DAD analysis of the mixture showed the presence of additional peaks (M1, M2, M3, M4, M5, M6, M7, M8) in addition to (+)-catechin and methyl-5-furfuraldehyde (Fig. 7), indicating that a reaction between (+)-catechin and methyl-5-furfuraldehyde occurred.

LC/MS analysis, performed in the negative ion mode, allowed molecular weight determination of the numerous products formed through this reaction. The obtained results indicated that these products were oligomeric derivatives consisting of (+)-catechin units bridged by methyl-5-furfuryl groups formed. The m/z values of compounds M1, M2, M3, M4, M5 and M6 detected at m/z 671 amu (Fig. 8a) showed that the constitutive units were linked by methyl-5-furfuryl bridges.

Mass spectrometry analysis revealed also the presence of that the two new compounds M7 and M8 all had molecular weights of 1054 amu ($[M-H]^-$ ion signals at m/z 1053 amu) (Fig. 8b) and corresponded to a structure in which three (+)-catechin are linked by two methyl-5-furfuryl bridge. They are trimer adducts.

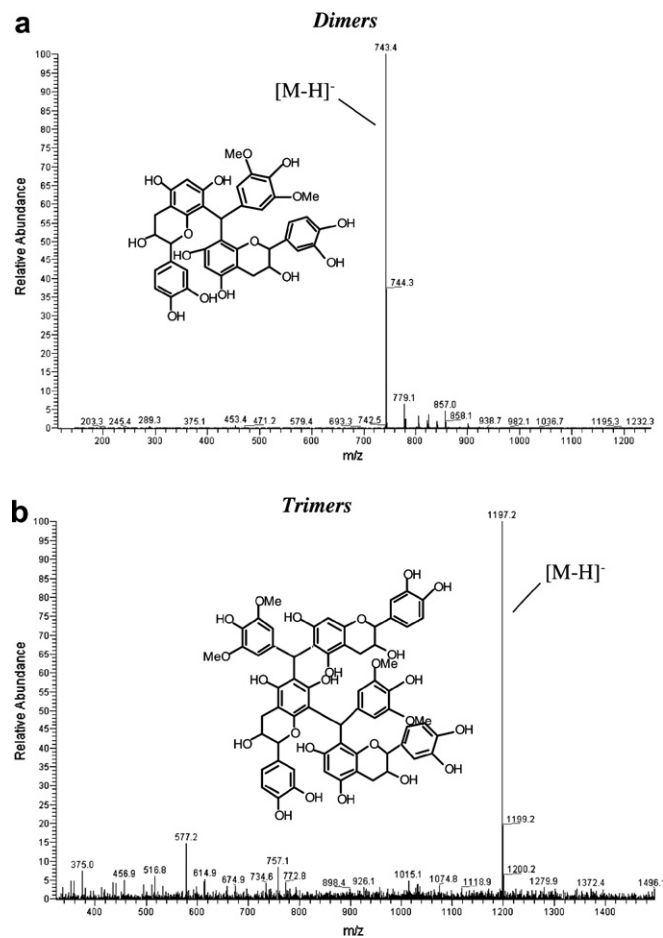


Fig. 11. Mass spectra of (a) dimer adduct of catechin–syringaldehyde and (b) trimer adduct of catechin–syringaldehyde.

A single ion monitoring (SIM) chromatogram profile (Fig. 9) recorded at m/z 1053 amu revealed the presence at 20 days of a third trimeric adduct: M9, and confirmed that M7, M8 are trimer adducts.

3.4. Reactions with syringaldehyde

HPLC technique (Fig. 10) permitted us to follow the reaction between (+)-catechin and syringaldehyde. A general decrease in the concentration of (+)-catechin and the appearance of numerous products initially absent in the mixture were observed.

The absorbance spectrum with a maximum at 280 nm showed that the formation of products conserved benzenic groups.

LC/MS analysis, conducted in the negative ion mode, allowed molecular weight determination of the five products formed through this reaction. Mass spectrometric analysis revealed that the compounds S1, S4, S5 gave all $[M-H]^-$ ion signals at m/z 743 amu as shown on the obtained mass spectrum (Fig. 11a). Their molecular weight

(744 amu) corresponds exactly to a structure in which two (+)-catechin units are linked by a syringaldehyde.

The same analysis revealed also that the compounds S2 and S3 gave $[M-H]^-$ ion signals at m/z 1197 amu (Fig. 11b). Their molecular weight (1198 amu) corresponds exactly to trimers: three (+)-catechin units are linked by two syringaldehyde: [catechin–syringaldehyde–catechin–syringaldehyde–catechin].

The compounds S6 and S7 were not ionisable under the conditions adopted in this experiment.

The evolution of the products (S1–S6) (Nonier et al., 2007) showed that the decrease of the initial products formed, which started at 25 days in the case of furfuraldehyde, did not start until 80 days in the case of syringaldehyde. However, with syringaldehyde these products were formed more slowly than with the furfuraldehyde. In addition, they accumulated, so it was not easy to obtain a polymerization reaction with this aldehyde family.

Single ion monitoring chromatogram profiles (Fig. 12) at m/z 743 amu and m/z 1197 amu confirmed the presence at 27 days of the dimer adducts: S1, S4, S5 and the trimer

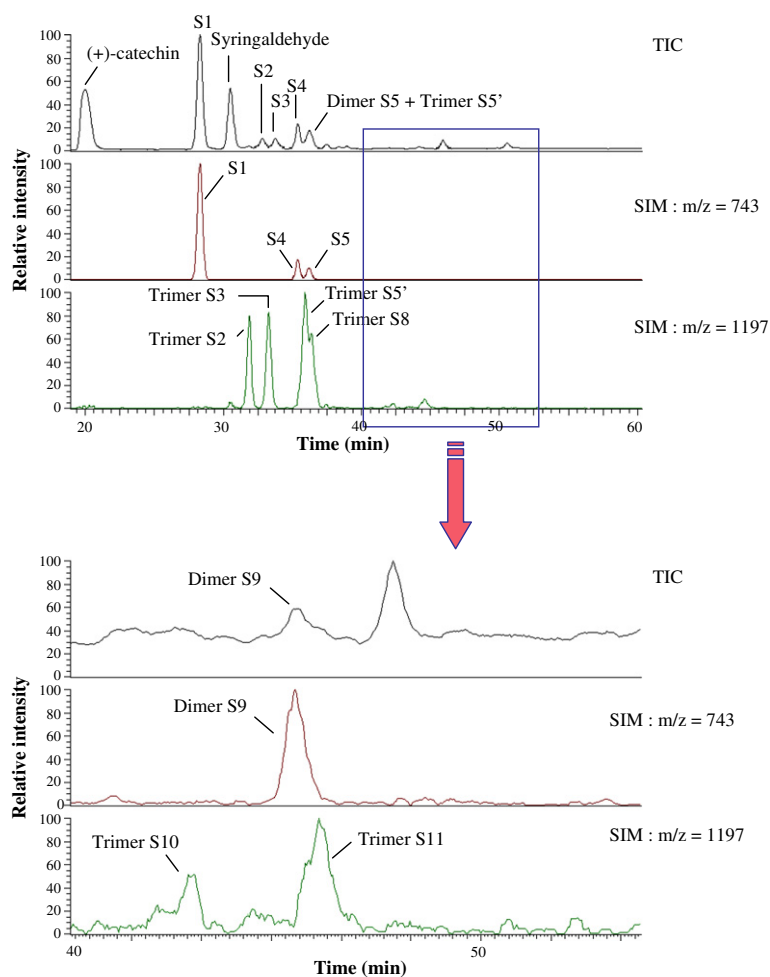


Fig. 12. Single ion monitoring chromatograms at m/z 743 and m/z 1197 during the syringaldehyde/(+)-catechin reaction performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

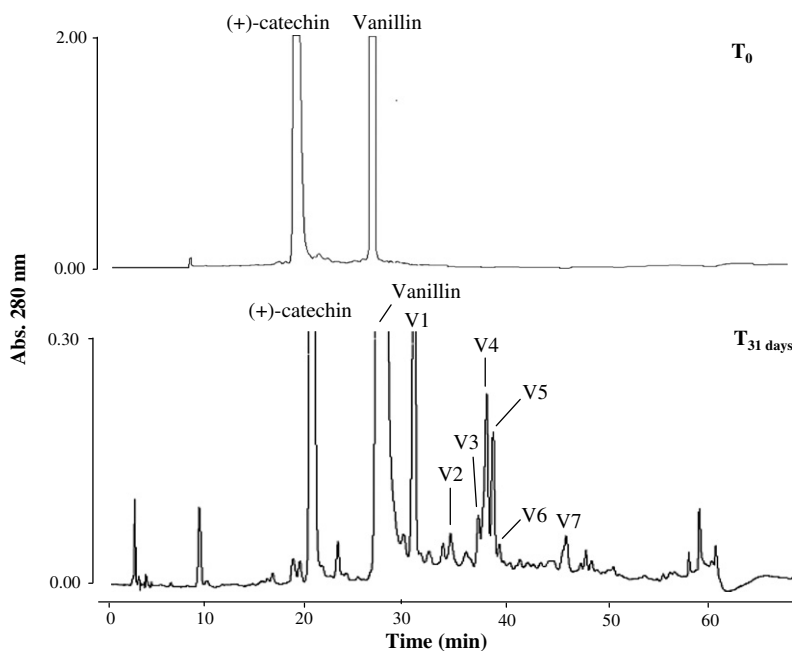


Fig. 13. HPLC chromatogram at 280 nm during the vanillin/catechin reaction. Reaction was performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

adducts: S2, S3. And they revealed the presence of four other trimers: S5', S8, S10, S11 and one other dimer: S9, no detectable in LC/DAD.

3.5. Reactions with vanillin

HPLC/DAD (Fig. 13) technique permits us to follow the reaction between (+)-catechin and vanillin in hydroalcoholic solution.

Less numbers of products appeared in the presence of vanillin than with syringaldehyde.

LC/MS analysis, conducted in the negative ion mode, allowed molecular weight determination of the five products formed through this reaction. Mass spectrometric analysis revealed that the compounds V1, V4, V5 gave all $[M-H]^-$ ion signals at m/z 713 amu as shown on the obtained mass spectrum (Fig. 14a). Their molecular weight (714 amu) corresponds exactly to a structure in which two (+)-catechin units are linked by a vanillyl.

The same analysis revealed also that the compounds V3, V6, V7 gave $[M-H]^-$ ion signals at m/z 1137 amu (Fig. 14b). Their molecular weight (1138 amu) corresponds exactly to trimers: three (+)-catechin units are linked by two vanillyl: [catechin–vanillyl–catechin–vanillyl–catechin].

Single ion monitoring chromatogram profiles (Fig. 15) at m/z 713 amu and m/z 1138 amu confirmed the presence at 31 days of the dimer adducts: V1, V4, V5 and the trimer adducts: V2, V3, V6, V7. And they revealed the presence of one other trimer: V8 no detectable in LC/DAD.

There was no bump at the end of the chromatogram indicating that there was no polymerization.

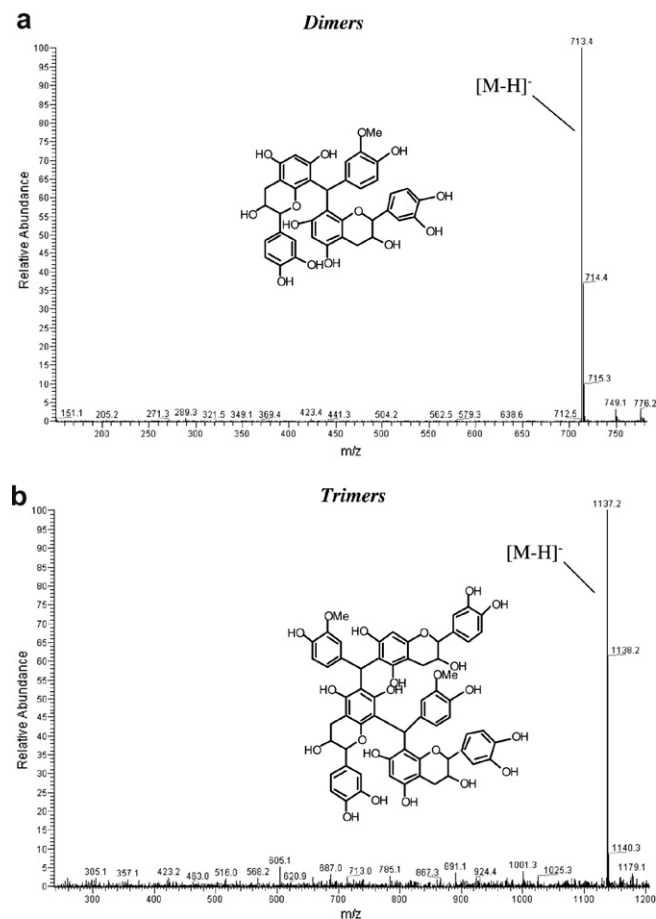


Fig. 14. Mass spectra of (a) dimer adduct of catechin–vanillin and (b) trimer adduct of catechin–vanillin.

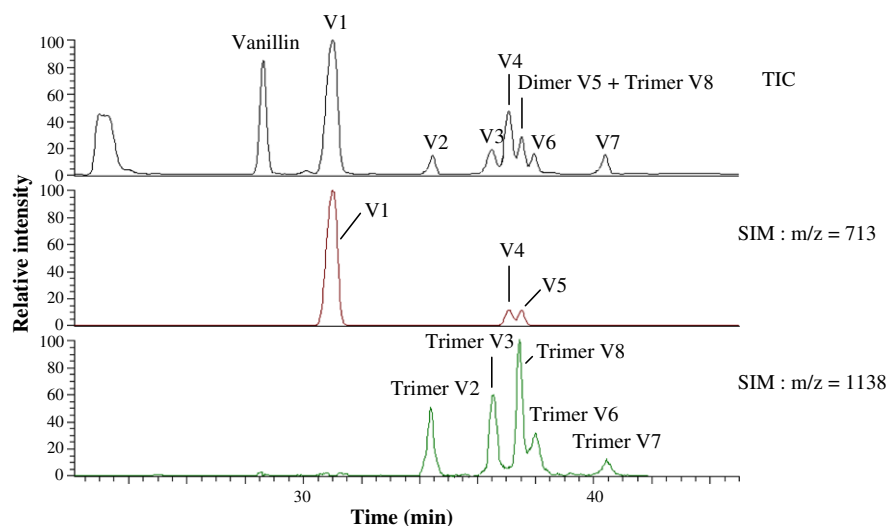


Fig. 15. Single ion monitoring chromatograms at m/z 713 and m/z 1138 during the vanillin/(+)-catechin reaction performed in hydroalcoholic solution (12% EtOH, 5 g/L tartaric acid, 1 N NaOH for pH adjustment) at pH 3.5.

Table 1
Principal condensation products of (+)-catechin and different oak wood aldehydes and their fragmentations

Aldehydes	Products [Kt-aldehyde-Kt] _n	[M-H] ⁻		Most abundant MS ion (70 eV), m/z (relative intensity)
		Calculated	Experimental	
Furfuraldehyde	$n = 1$	657.2	657.4	657 (100)
	$n = 2$	1025.3	1025.4	1025 (100)
	$n = 3$	1393.3	1393.1	1393 (14) 1105 (12) 1025 (100)
Hydroxymethylfurfuraldehyde	$n = 1$	687.2	687.3	687 (100)
	$n = 2$	1085.2	1085.2	1085 (42) 669 (100)
Methyl-5-furfuraldehyde	$n = 1$	671.1	671.1	671 (100)
	$n = 2$	1053.2	1053.1	1053 (100)
Syringaldehyde	$n = 1$	743.2	743.4	743 (100)
	$n = 2$	1197.3	1197.2	1197 (100)
Vanillin	$n = 1$	713.2	713.4	713 (100)
	$n = 2$	1137.3	1137.2	1137 (100)

For summarize, we presented in Table 1 the principal condensation products of (+)-catechin and different oak wood aldehydes and their fragmentations.

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