SUPPLEMENTARY MATERIAL TO

Hydrothermal hydrolysis of sweet chestnut (*Castanea sativa*) tannins

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Figure S1 depicts the typical chromatograms of: the A- initial material, B- water-soluble product, obtained at temperature of 150 °C and reaction time of 30 min, C- water-soluble product, obtained at temperature of 250 °C and reaction time of 30 min and D- sample obtained by acid hydrolysis. As can be observed from chromatograms, the detected peaks represent gallic and ellagic acids and ellagitannins, such as vescalin, castalin, vescalagin, castalagin and 1-o-galloyl-castalagin. The tannins were determined based on the data published by Comandini *et al.*[1] and obtained UV spectrums. Comparing chromatograms A and B from Figure S1, it can be noticed that using water at mild conditions (150 °C and 30 min) the ellagitannins content already decreased and the concentration of ellagic acid starts to increase slightly, while gallic acid was still stable. Observing Figure S1C, it is obvious that there are no gallic acid and elagitannins anymore in the product, but concentration of ellagic acid drastically increased. Figure S1D shows that gallic acid and ellagitannins are not stable at conditions of acid hydrolysis and they are present in very small amount in that product. It also can be noticed that ellagic acid was the predominant compound in product obtained by acid hydrolysis.

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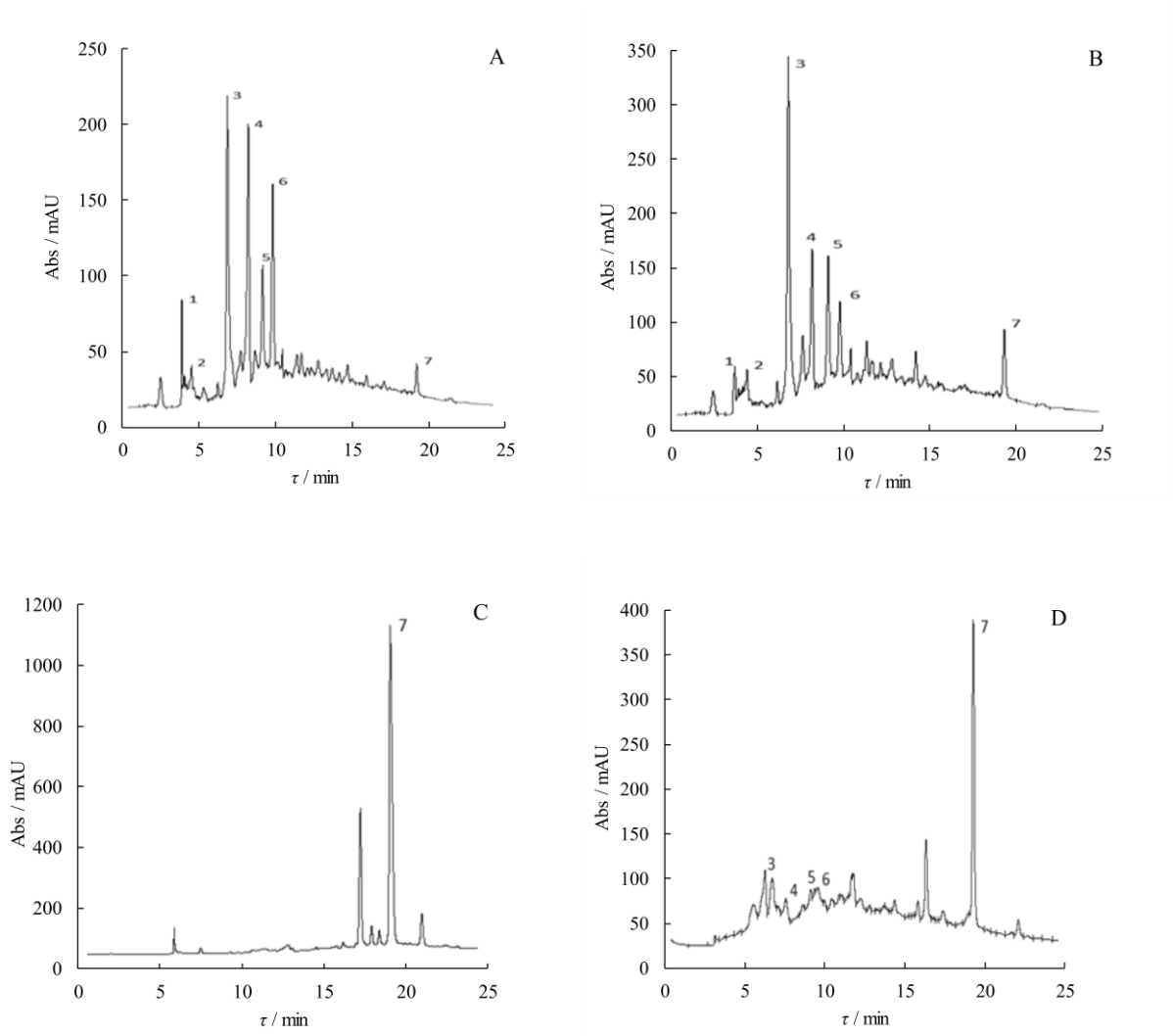

Figure S1. Typical chromatogram of: A - initial tannin extract; B - chestnut tannin extract treated with water at temperature of 150 ºC and reaction time of 30 min; C - chestnut tannin extract treated with water at temperature of 250 ºC and reaction time of 30 min; D - acid hydrolized chestnut tannin extract. Detected compounds: 1-vescalin, 2-castalin, 3-gallic acid, 4-vescalagin, 5-1-o-galloyl castalagin, 6-castalagin, 7-ellagic acid.

Figure S2 describes the proposed mechanism of degradation of sweet chestnut tannin extract by subcritical water and the formation of important products.[2–5] Ellagitannins are biologically formed from pentagalloyl-glucose (gallotannin).[3] Canas *et al.* assumed that the gallic acid is a product of the hydrolysis of some galloyl esters associated with the parietal composites of chestnut cells.[6]

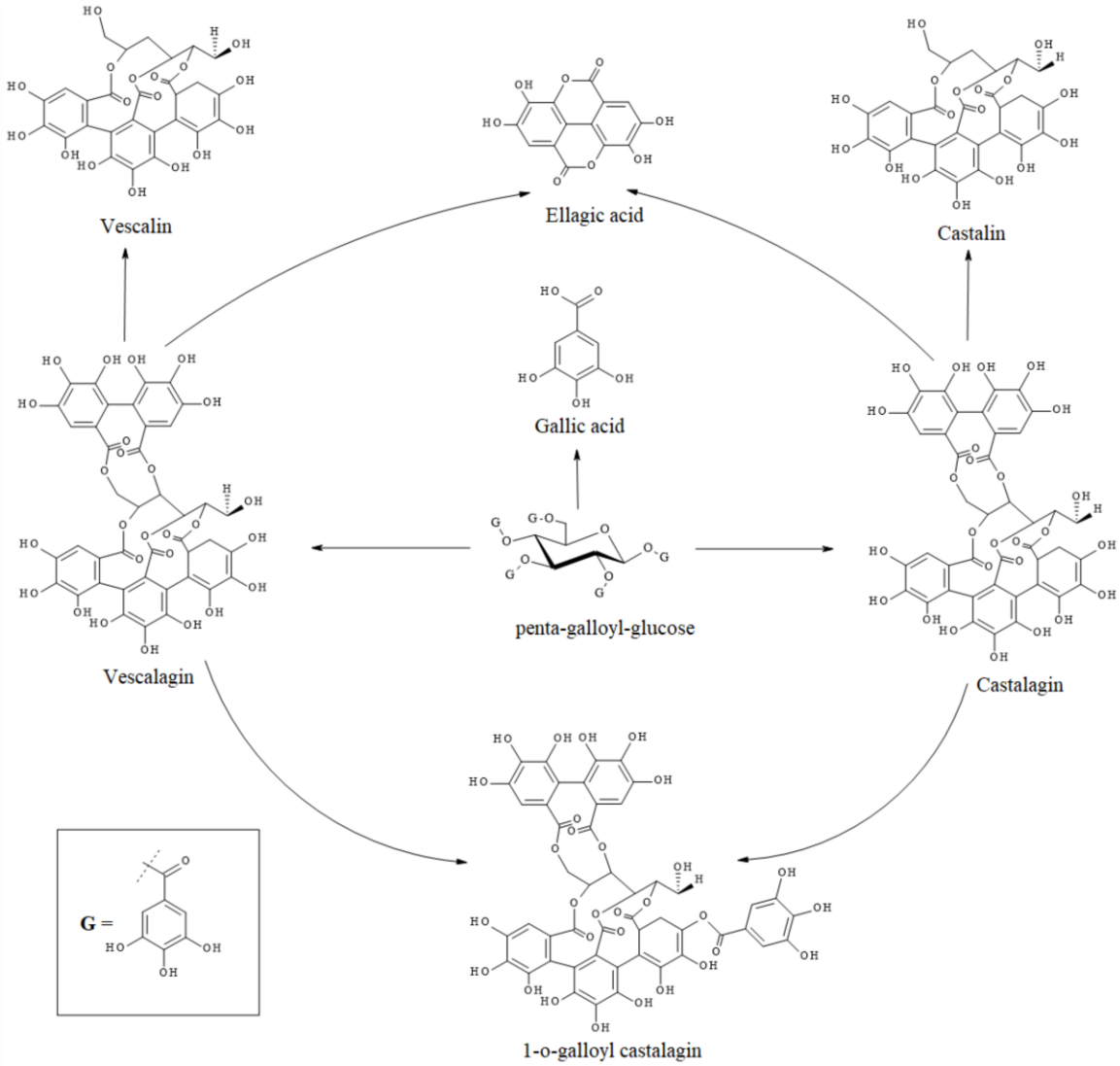

Figure S2. The proposed mechanism of sweet chestnut tannins reaction in subcritical water.

Vescalagin and castalagin are two aromatic glycosides with 4,6-hexahydroxydiphenyl coupling and an unique flavogallonyl group which is composed of three galloyl groups linked together with C-C bonds.[2] The presence of vescalin and castalin is caused by hydrolysis of hexahydroxydiphenyl unit of vescalagin and castalagin.[2] Ellagitannins are converted into ellagic acid by intra-molecular esterification reaction of hexahydroxydiphenic acid.[7] 1-o-galloyl castalagin is hydrolysable tannin previously identified in Eugenia grandis.[8] Comandini *et al.* deducted that this molecule can be formed by esterification of castalagin or vescalagin with a gallic acid residue.[1]

It was proved that vescalagin and castalagin can react with itself to produce oligomeric ellagitannins, such as roburin A and roburin D (dimers of vescalagin and castalagin, respectively).[9]

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