

# STRUCTURES AND SENSORY ACTIVITY OF MOUTH-COATING TASTE COMPOUNDS FORMED BY ELLAGITANNIN TRANSFORMATION DURING OAK WOOD TOASTING USED IN BARREL MANUFACTURING

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## Abstract

Aimed at investigating the chemical and sensory changes of ellagitannins during toasting of oak barrels, the native ellagitannins castalagin and vescalagin have been thermally treated in model systems after isolation from oak wood by means of gel permeation chromatography and HPLC. Depending on their stereochemistry at the C1 carbon atom of the glucose core, these astringent ellagitannins are degraded via different pathways into less mouth-coating taste compounds. These compounds then act as transient intermediates, which are further converted into deeply golden-brown coloured, melanoidin-type macromolecules. For example, the *S*-configured castalagin is oxidised to the previously not reported dehydrocastalagin, whereas the *R*-configured vescalagin, is converted into deoxyvescalagin, which means that both compounds show a complete different reaction pattern based on their stereochemistry.

## Introduction

Wines and spirits such as whiskey are matured in toasted oak barrels for extended periods to give the beverages the desirable aroma, taste, and colour. Some of the native oak wood compounds are well characterised [1,2] and the toasting of oak wood is commonly known as one of the most important steps inducing the formation of taste and browning compounds by thermal degradation of wood constituents (e.g. ellagitannins). Nevertheless the structures of taste-active non-volatiles generated during oak wood toasting remain mainly unknown. Therefore, the chemical nature and sensory activity of reaction products produced in toasting model experiments were studied.

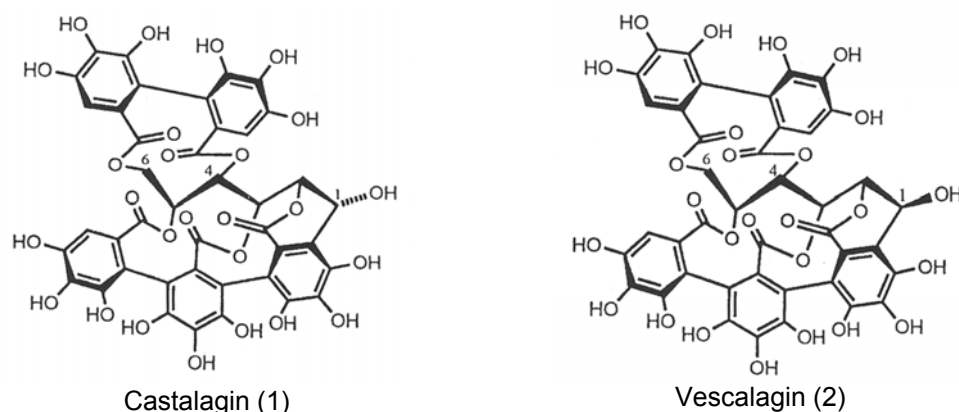
## Experimental

Castalagin (**1**) and vescalagin (**2**) were extracted from oak wood chippings with 70% aqueous methanol and purified by means of gel permeation chromatography (GPC) using LH-20 material, followed by preparative RP-HPLC as described elsewhere [3]. The purified ellagitannins were placed in a glass vial and thermally treated in a lab oven for up to 60 min at 175°C. After cooling, the toasted samples were taken up in water and analysed by RP-HPLC/DAD. The formed degradation products were isolated by means of prep. HPLC and then identified by means of LC-MS/MS and 1D/2D-NMR experiments [4].

## Results and Discussion

Samples of purified castalagin (**1**) and vescalagin (**2**) (Figure 1), isolated from oak wood chippings, were thermally treated at 175°C. After taking up the reaction mixture in water, the product profile of both reaction mixtures was monitored by means of HPLC-DAD. A “hump” of mouth-coating, brown coloured, melanoidin-type polymers (CP) was detected as well as ellagic acid (E), indicating a thermohydrolytic cleavage of the ellagitannins. In addition, individual major reaction products were produced upon toasting of **1** and **2** besides residual amounts of non-reacted ellagitannins as outlined in Figure 2. After isolation of **T1** and **T2** the following LC/MS/MS and 1D/2D NMR experiments interestingly showed that **1** was oxidized to the previously not reported dehydrocastalagin (**T1**) strongly depending on the stereochemistry. Its diastereomer **2**, just differing at the C1 carbon atom of the glucose core, is surprisingly converted into deoxyvescalagin (**T2**) (Figure 2). Similar results for this stereo-guided reaction pattern were found for the hydrolysis products castalin and vescalin, lacking the ellagic acid unit, as well as for the dimers roburin D (casta-configuration) and roburin A (vesca-configuration). These results prove that the C1 stereo chemistry is the key driver for the reaction upon thermal treatment regardless of the molecule size.

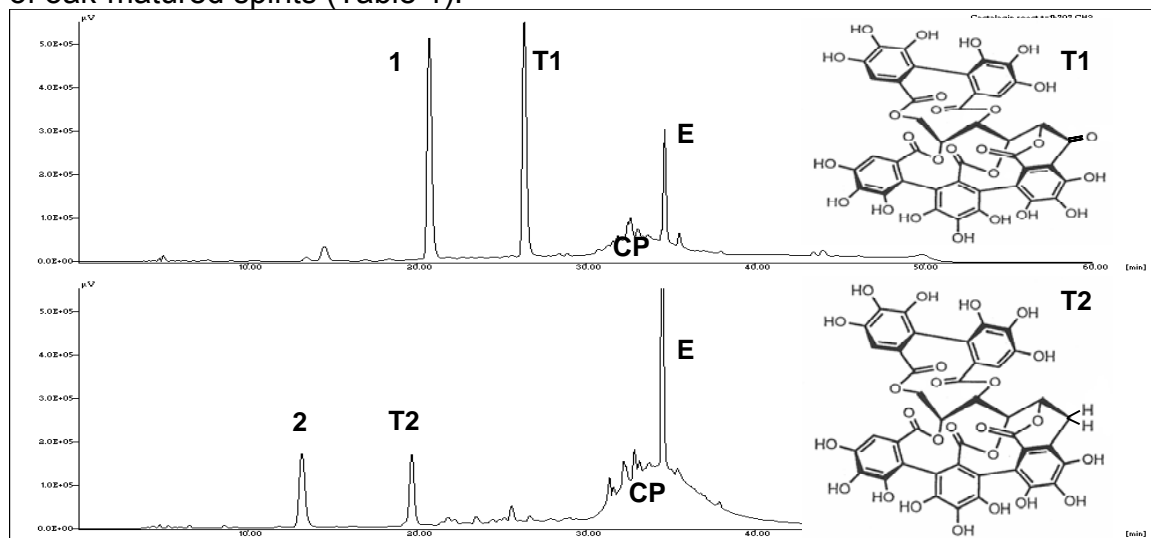
Comparison of both reaction mixtures revealed also major differences in their thermo-stability with **1** as the more stable isomer and **2** as an excellent precursor for mouth-coating polymers, being converted more rapidly and effectively into polymeric structures.



**Figure 1.** Structure of castalagin (1) and vescalagin (2).

In order to investigate the impact on the taste the sensory properties of the ellagitannin transformation products **T1** and **T2** were determined by means of an expert panel and compared to those of the native ellagitannins **1** and **2**. These sensory studies revealed taste thresholds for astringency of 1.1 µmol/L for both **1** and **2** whereas the thermal metabolites **T1** and **T2** were evaluated with somewhat higher thresholds of 4.4 and 3.3 µmol/L, respectively. The isolated polymers CP exhibited a mouth-coating oral sensation at a threshold concentration of 13.8 mg/L. As their oak-derived precursor ellagitannins **1** and **2** both imparted strong astringency at the low taste threshold of 0.9 mg/L each, it might be concluded that the toasting process is converting the highly astringent ellagitannins into less puckering, mouth-coating

substances. Thus this conversion might contribute to the balanced gustatory profile of oak-matured spirits (Table 1).



**Figure 2.** RP-HPLC chromatogram after thermal treatment of 1 and 2 (60 min, 180°C).

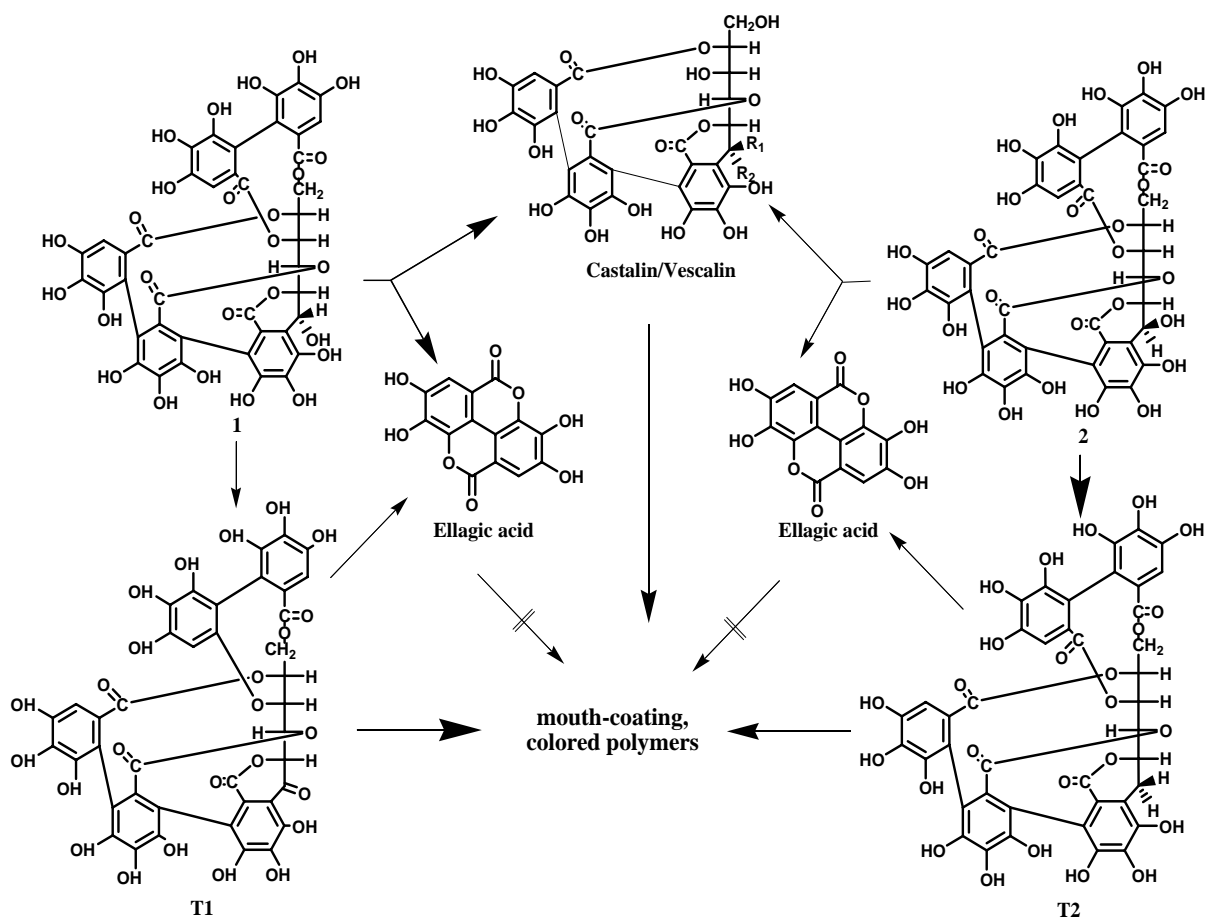
**Table 1.** Taste thresholds of native ellagitannins and their degradation products.

Compound	Threshold in $\mu\text{mol/L}$	Threshold in $\text{mg/L}$
Castalagin (1)	1.1	1.0
Vescalagin (2)	1.1	1.0
Dehydrocastalagin (T1)	4.4	4.1
Deoxyvescalagin (T2)	3.4	3.1
Polymeric hump	-	13.4

Based on quantitative model experiments (data not shown) the formation of the coloured oligomers might occur via two alternative pathways. On the one hand 1 and 2 are converted by oxidation respectively reduction into the transient intermediates T1 and T2 which then rapidly further undergo degradation to yield mouth-coating, melanoidin-type polymers. On the other hand castalagin and vescalagin, formed upon thermohydrolytic cleavage of ellagic acid from 1 and 2 and as such of low taste activity, were found as potential intermediates in polymer generation (Figure 3).

## Conclusions

During oak wood toasting the astringent native ellagitannins are converted into less astringent metabolites. These metabolites were identified as transient intermediates of thermal transformation of ellagitannins into mouth-coating melanoidin-type polymers which contribute to the colour and balanced taste of oak matured beverages. These studies offer insights into the complex ellagitannin transformation chemistry and give some molecular explanation for the change of sensory-active non-volatiles in oak wood during toasting inducing the desired balanced, smooth taste of oak matured spirits.



**Figure 3.** Degradation pathways of 1 and 2 upon thermal treatment.

## References

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