



# Organic compounds in olive mill wastewater and in solutions resulting from hydrothermal carbonization of the wastewater



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## HIGHLIGHTS

- Organic components of native olive mill wastewater were analyzed by GC–MS.
- Tyrosol, hydroxy-tyrosol and aglycons proved most abundant in native OMW.
- Components of native OMW were compared to hydrothermally carbonized OMW.
- Complex aglycons and lipids were hydrolyzed during hydrothermal carbonization.

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## ABSTRACT

Organic components in olive mill wastewater (OMW) were analyzed by exhaustive solvent extraction of the lyophilisate followed by pre-chromatographic derivatization techniques and GC/MS-analysis of the extracts. Simple biophenols including tyrosol (Tyr), hydroxytyrosol (OH-Tyr) and homovanillic alcohol as well as complex biophenols including decarbomethoxy ligostride aglycon and decarbomethoxy oleuropein aglycon proved most abundant analytes. Hydroxylated benzoic and cinnamic acids are less abundant, which may indicate a humification process to have occurred. The pattern of organic components obtained from native OMW was compared with that obtained from hydrothermal carbonization (HTC) of the waste product. Former results provided strong evidence that HTC of OMW at 220 °C for 14 h results in an almost complete hydrolysis of complex aglycons. However, simple biophenols were not decomposed on hydrothermal treatment any further. Phenol and benzenediols as well as low molecular weight organic acids proved most abundant analytes which were generated due to HTC. Similarly to aglycons, lipids including most abundant acylglycerines and less abundant wax esters were subjected almost quantitatively to hydrolysis under hydrothermal conditions. Fatty acids (FAs) released from lipids were further decomposed. The pathways of volatile analytes in both native OMW and aqueous HTC solutions were studied by solventless headspace-Solid Phase Micro Extraction. Basically, a wide array low molecular alcohols and ketones occurring in native OMW survived the HTC process.

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## 1. Introduction

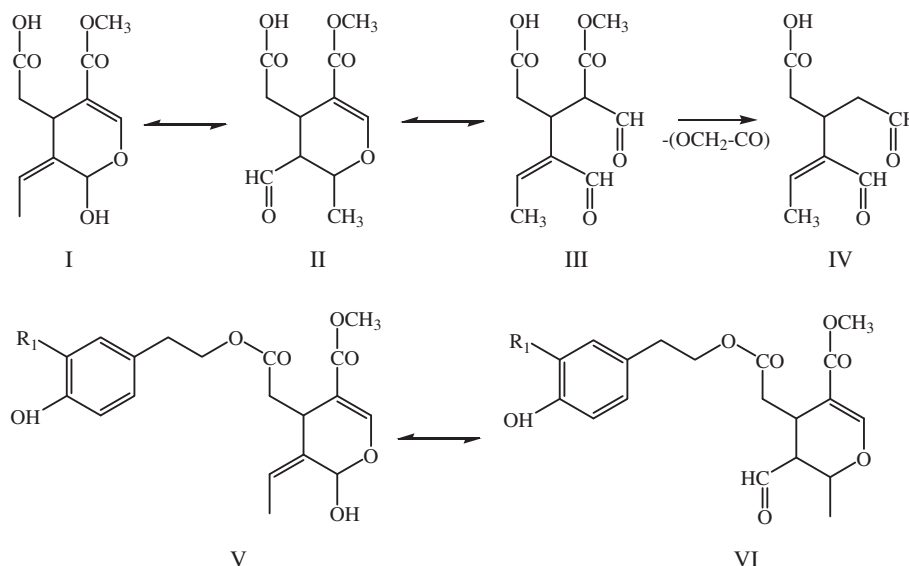
The hydrothermal treatment of OMW was studied in a previous paper (Poerschmann et al., 2013). HTC is an environmentally sound single-step thermochemical conversion of biomasses. The aqueous biomass (dry substance matter ~10% w/w in case of OMW) was allowed to react in subcritical water at 220 °C for 14 h. Normally, the primary objective of HTC is the production of biochar (Titirici and Antonietti, 2010), which can be used for energetic reasons or for soil improvement. In the special case of OMW, a remediation purpose of the hazardous waste product is associated. As known, the wastewater is characterized by high chemical oxygen demand

(COD) and high biochemical oxygen demand (BOD), exceeding corresponding data for sewage by far (El-Abbassi et al., 2012). The bulk parameters COD and BOD can vary due to extraction of olives, processing and storage. In olive mills, the extraction is performed either by a (traditional) discontinuous press or a solid/liquid centrifuge. Both processes result in the production of two waste streams: olive mill residual solids and OMW. HTC with the waste product OMW may have promising prospects regarding the better accessibility of aqueous HTC solutions to biogas/biofuel production as well as their better accessibility to selective extraction of valuable phenols as compared to the native OMW.

A wide array of organic compounds could be identified in the aqueous HTC solution rich in dissolved organic matter (DOM) (Poerschmann et al., 2013). Aromatic alcohols including OH-Tyr, Tyr and homovanillic alcohol were found to be very abundant

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**Scheme 1.** Keto-enol tautomeric equilibrium of elenolic acid and aglycons ( $R_1 = \text{H}$ : Tyr,  $R_1 = \text{OH}$ : OH-Tyr) I-elenolic acid in closed ring hemiacetal structure ( $\text{C}_{11}\text{H}_{14}\text{O}_6$ , MW = 242 Da), II-monoaldehydic form of elenolic acid, III-dialdehydic form of elenolic acid, IV-dialdehydic form of decarboxy methyl elenolic acid, V-ligostride aglycon ( $R_1 = \text{H}$ ,  $\text{C}_{19}\text{H}_{22}\text{O}_7$ , MW = 362 Da), and oleuropein aglycon ( $R_1 = \text{OH}$ ,  $\text{C}_{19}\text{H}_{22}\text{O}_8$ , MW = 378 Da), VI-monoaldehydic forms of ligostride aglycon and oleuropein aglycon.

compounds. Whereas the structural characterization of virgin olive oil<sup>1</sup> has widely been addressed so far (see Bendini et al., 2007 and references cited therein), information about OMW on the molecular level along with quantification of organic compounds have been scarce. Characterization of OMW has commonly been performed on the basis of bulk parameters chiefly aimed at tracing its microbial conversion, abiotic degradation or purification by sorbents (see Justino et al., 2010 and references cited therein).

Organic compounds of virgin olive oil are grouped into (i) benzoic acids and derivatives, (ii) cinnamic acids, (iii) phenyl ethyl alcohols, (iv) other phenolic acids, (v) flavonols, flavones, lignans, and isochromans, and (vi) secoiridoids (Bendini et al., 2007). Prominent surrogates of the latter group, which are known for antioxidative and radical scavenging features as well as bitter taste, include the dialdehydic form of elenolic acid linked to Tyr (decarboxymethoxy ligostride aglycon) and to OH-Tyr (decarboxymethoxy oleuropein aglycon) as well as oleuropein aglycons (Tripoli et al., 2005; Obied et al., 2009). Secoiridoids in the aglyconic form result from glycosides in the olive fruit by enzymatic hydrolysis via endogenous  $\beta$ -glucosidases such as polyphenol oxidase and peroxidase activated as a result of crushing and malaxation (Vierhuis et al., 2001). The formed aglycons are subjected to keto-enol tautomeric equilibrium that involves ring opening (Di Donna et al., 2011). Scheme 1 depicts the hemiacetal structure of elenolic acid (I) that equilibrates into the monoaldehydic dihydropyran form (II) and the more stable dialdehydic form (III) as well as into the dialdehydic form lacking a carboxymethyl group (IV). Correspondingly, structure V indicates the ligostride aglycon ( $R_1 = \text{H}$ ; tyrosilenoate) and oleuropein aglycon ( $R_1 = \text{H}$ ; hydroxytyrosilenoate) in the OH-form, structure VI indicates the corresponding monoaldehydic form (De Nino et al., 2000). The (ring-opened) dialdehydic isomer (III) prevails over the substituted dihydropyran (II) at a ratio of about 3:1 (Bendini et al., 2007). Further hydrolysis of aglycons during subsequent processing gives rise to the release of simple phenols including Tyr and OH-Tyr (Servili et al., 2004).

Since HTC is a relatively new technique and OMW has not been

applied as feedstock for detailed HTC studies so far, the fate of organic compounds occurring in native OMW during the HTC process has not been addressed either. As an example, it remains to be clarified yet, to which degree simple biophenols are decomposed and if simple biophenols are completely released from complex aglycons by virtue of the HTC procedure. The elucidation of pathways of intrinsic organic compounds in native OMW during the hydrothermal process is expected to foster understanding and optimizing the HTC process.

To study their fate, intrinsic organic compounds in native OMW were identified and quantified in the framework of this contribution. Afterwards, this organic compound pattern in native OMW was compared to that obtained by extracting the HTC matrix. Target compound classes include aromatic alcohols and acids, aliphatic alcohols and acids, oxygen-functionalized analytes including ketones, aldehydes and analytes with heteroatoms (N, S). The analytical protocol was characterized by exhaustive solvent extraction and alkaline saponification of lyophilisates of native OMW followed by derivatization of the extracts and GC/MS-analysis. To compare patterns of analytes, the corresponding data for HTC solutions were taken from Poerschmann et al. (2013).

## 2. Materials and methods

### 2.1. Chemicals

All chemicals applied in the framework of this contribution were reagent or analytical grade. A wide array of isotopically labeled internal standards was used: phenol- $d_6$ , hydroquinone- $d_4$ , 4-M-catechol- $d_3$  (M: methyl throughout the text), n-amylalcohol- $d_{12}$ , palmitic acid- $d_2$ , succinic acid- $d_4$ , phenanthrene- $d_{10}$ . Internal standards were purchased from CIL (Cambridge Isotope Lab., Andover/MA). Beyond, an array of non-labeled authentic standards which cover a wide range of polarity and hydrophobicity (Poerschmann et al., 2013), was used. Derivatization agents included BSTFA (N,O-bis(trimethylsilyl) trifluoroacetamide) and MTBSTFA to generate trimethylsilyl (TMS) derivatives and t-butyl dimethylsilyl derivatives, respectively, as well as boron trifluoride ( $\text{BF}_3$ ) methanol (14% w/w) to produce methyl esters. All of them were

<sup>1</sup> The description "virgin" characterises the oil extracted from olive fruits by mechanical extraction only, thus avoiding any thermal and chemical treatment.

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